An Environmentally Friendly Alternative for The Conventional Acids Used in Matrix Acidizing and Acid Fracturing of Carbonate Reservoirs

By

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Abstract

Oil and gas industry has been using acidizing techniques in carbonate formations to remove unwanted substances, reconnect the flow path and introduce a new flow channel in order to increase oil production. These techniques have been developed and applied to maximize oil production while bypassing the near wellbore damage. Commonly used acids such as hydrochloric acid (HCl) and hydrofluoric acid (HF) damage equipment. Furthermore, their additives such as corrosion inhibitors, surfactants, and iron control agents are harmful to oil field workers and they are not environmentally friendly. Moreover, transportation of such fluids to the well-head and neutralization of the flow-back products is costly.

The Ultra Series FF-01 is both an environmentally and equipment friendly alternative to the products available in the market presently. The Ultra Series FF-01 is very acidic, its pH is less than 1, and has a slower reaction rate compared to HCl. It can work up to 72 times longer than hydrochloric acid. Most importantly, it is biodegradable and is non-corrosive to the field equipment.

The main objective of this study is to compare the ability of Ultra Series FF-01 in generating worm holes and etching fracture surfaces with the conventional acidizing fluids used for well stimulation. Experiments were divided into seven parts namely beaker testing for corrosion, beaker testing for reaction rate, beaker testing for emulsion, interfacial tension measurement, viscosity testing by Brookfield viscometer, matrix acidizing tests, and acid fracture conductivity measurement tests.

The beaker test was used for studying the effect of the sample acid on the stainless rod. The study shows a mass reduction of the stainless steel rod after it was in the beaker with 15% HCl while there is no mass loss for a stainless rod in the Ultra Series FF-01 after 24 hours. Furthermore,

beaker test shows the Ultra Series FF-01 has a slower reaction rate than 15% HCl and creates less emulsion when compared it with 15% HCl and 15% HCl with additives.

Viscosity testing by Brookfield viscometer was performed to compare the viscosity of the crude oil after mixing it with acidic solution samples. The experiment shows that the viscosity of the crude oil at the interface with the Ultra Series FF-01 was lower when it was compared with the samples that were collected at the interface of 15% HCl and the crude oil. In addition, the interfacial tension (IFT) test shows a declining of interfacial tension value when the concentration of the Ultra Series FF-01 increased.

A core flooding setup was used to compare the ability of Ultra Series FF-01 with the conventional acidizing fluid in increasing the permeability of limestone core samples for matrix acidizing applications. The results show that Ultra series FF-01 produced better results than 15% HCl without additives, when the permeability of the core samples was less than 5 mD and the injection rate used in the experiment was 0.5 mL/min. The Ultra Series FF-01 was able to generate wormholes in low permeability cores at low injection rates. On the contrary, 15% HCl with stronger dissolution capability at the surface of the core sample, was unable to generate wormholes under the same condition. However, 15% HCl with commercial additives (the iron control agent, non-emulsifier, and corrosion inhibitors) showed superior results when used as the acidizing fluid for all ranges of injection rates and permeability.

Acid conductivity measurement tests were designed to simulate acid fracturing for comparing the performance of different acid fracturing fluids. The two acid fracturing fluid types that were used in these experiments are Ultra series FF-01 and conventional 15% hydrochloric acid with its commercial additives. Conductivity after etching by the Ultra series FF-01 was significantly better compared to that obtained with 15% hydrochloric acid with additives, for all values of closure

stress, when the leak off pressure was set at 100 psi lower than the system pressure. The etching patterns generated by the two fluids are evidently different. The etching pattern created by the Ultra series FF-01 was in the shape of human veins and were both visible and connected. In contrast, the surface of the core samples that were etched by 15% hydrochloric acid with additives, were bouncy but shallow, producing inferior conductivity. In addition, the performance of the Ultra series FF-01 was slightly better than 15% hydrochloric acid with additives, when the leak off pressure was set at 50 psi lower than the system pressure, for all closure stress values except for 1000 psi.

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1. Introduction

Acidizing is a well treatment technique that has been used in oil industry to increase oil productivity. Acidizing treatments are mostly performed in carbonate reservoirs. The key part of the acidizing technique is to inject an acidic solution into the well to dissolve unwanted residue inside and/or around the wellbore. A commonly used acid for acidizing treatments is hydrochloric acid. It is normally diluted to 15%. In some cases, it is used in higher concentrations in order to have an effective treatment. Hydrochloric is a highly reactive acid. The reaction rate is higher when reactions take place at higher temperature. Thus, well treatments in tight and/or high temperature formation are facing a difficulty in producing good results when hydrochloric acid is used as the main acid for well acidizing. Furthermore, hydrochloric acid is a toxic chemical according to OSHA. In some cases, it could even result in death [1]. Hydrochloric acid is not the only chemical used in well acidizing. There are many other chemicals that are used as additives to enhance the ability of the acidizing fluid to achieve the desired results of high conductivity or permeability after the treatment [2]. According to a study by Abdullah et al [3], there are close to 300 chemicals that are used during well acidizing. Some of them are categorized as toxic and deadly to the living matter. An alternative for the conventional acid solution used for acidizing has been studied which would not only improve production and prevent corrosion, but also helps in minimizing the negative impacts on human's health and the environment caused by the large amount of chemical toxin left back in the reservoir formation during acidizing [4, 5, 6, 7].

The objective of this research is to study the ability of the Ultra Series FF-01 to substitute the conventional HCl acid used in well acidizing. The Ultra Series FF-01 will be tested for rate of reaction comparison with 15% HCl. Then it will be tested as a matrix acidizing fluid using a core flooding setup. Simulation of matrix acidizing will be carried out to test the efficiency of sample

acid solutions including the Ultra Series FF-01, 15% hydrochloric acid, 15% hydrochloric acid with additive, 10% acetic acid, and the mixture of the Ultra Series FF-01 and 15% hydrochloric acid. In addition, a sensitivity analysis of operating parameters, like injection rate, temperature, applied back pressure etc., was carried out to optimize matrix acidizing by using Ultra Series FF-01. Finally, the increase in the permeability factor after acidizing time is complete, will be compared for each test.

Moreover, the Ultra Series FF-01 will be tested as an acid fracturing fluid with carbonate rock samples using a fracture conductivity setup. Conductivity results will be compared for different closure stress values and the surface pattern created by reaction during acidizing will be examined. Ultra-Series FF-01 and 15% hydrochloric acid, along with the additives, will be used for this experiment. Since the fractures are relatively long and far away from the well bore, part of the acid is likely to be spent at the entrance of the fracture as acid moves along the formation before it reaches the fractures tip. Therefore, a reactor with a carbonate rock inside is added to replicate the field situation. The results of the acid conductivity experiment with the Ultra Series FF-01 will be compared to the results produced by using 15% HCl with additives.

The change of viscosity of the crude oil and formation of emulsion after acidizing is a matter of concern impacting the outcome. The thickening crude oil and emulsion can potentially reduce the ability of the crude oil to flow easily to the well bore. Thus, the rheology study is needed. The viscosity test will be performed by the Brookfield viscometer to determine the viscosity at the interface of the sample acidizing fluids and the sample crude oils. Also, the beaker test will be performed to see whether the Ultra Series FF-01 will form an emulsion after it comes to contact with the sample crude oil. In addition, the IFT test will be used to see the change of the interfacial tension values when the Ultra Series FF-10 contact the sample crude oil.

Lastly, the beaker test will be used to test the effect of the Ultra series FF-01 and 15% hydrochloric acid on the stainless steel rod. [6].

2. Literature review

This section will summarize earlier works published on alternatives to conventional acid solutions and also a brief history of Ultra Series FF-01. There are six sections in this chapter which are listed below:

- 2.1 Introduction to well acidizing techniques
- 2.2 Chemistry of conventional acid solutions used for acidizing
- 2.3 Previous study of the conventional acids and their alternative solutions used for acidizing
- 2.4 Corrosion of the field equipment
- 2.5 Environmental impact of the acidizing solutions
- 2.6 An introduction to Ultra Series FF-01
- 2.7 Matrix acidizing tests
- 2.8 Acid conductivity measurements

2.1 Introduction to well acidizing techniques

Lower productivity as a result of formation damage or naturally low permeability can be stimulated by acidizing hydrocarbon-bearing formations. Well stimulation by acid treatment was first introduced to the petroleum industry by Standard Oil Co.'s Solar Refinery in 1895. Standard oil Co.'s method was an acid treatment for a carbonate formation well in Lima, Ohio using hydrochloric acid. Herman Frasch, a chemist there was credited as the inventor for this acidizing

procedure. In 1896, a patent was issued to Frasch which is the earliest patent for acidizing. It is beneficial for modern acidizing as many methods of acid treatment are derived from this well-known technique [8, 9].

Well treatment by acidizing has been a successful method to stimulate oil production. However, the technique has the disadvantage of causing corrosion of field equipment and piping, due to the high corrosive rate of hydrochloric acid. Well stimulation with acid solutions became a more acceptable method to the oil industry, once Dow Chemical added arsenic to inhibit the reaction of hydrochloric acid to the metal and a treatment for several dead wells was success in Michigan [10, 11]. Several acidizing treatment techniques developed from that point and this technique became a commonly used well stimulation technique in the present oil industry. The goal of the treatment surely is to improve the productivity, though choosing a proper method for treatment is critical. The acidizing process can be categorized into three processes which are acid washing, matrix acidizing and acid fracturing. These processes could be effective if the reservoir is carefully studied and the appropriate treatment is applied to the formation.

The first of acidizing methods is acid washing. This method is used to improve oil production by removing unwanted substances from the piping or well bore such as asphaltene build up, scale accumulation, paraffin wax deposition and/or debris remaining from perforation. This clean-up process is done by injecting acid into the wellbore and allowing it to dissolve the undesirable matter in the area that is plugged or clogged [8].

The second acidizing treatment is matrix acidizing. This treatment is performed in a well that is damaged or has a positive skin around the wellbore. The treatment is completed by injecting acidizing solution into the reservoir with a pressure that is less than the formation fracture pressure. Acid solution dissolves part of soluble formation and penetrates into the reservoir. The process re-

connects pores, enlarges previous flow channels and creates new wormholes. These remove positive skin and increase the permeability of the formation around the well bore area. Compared to acid fracturing, this method is the preferred method in a reservoir that is close to an aquifer or gas source to avoid breaking into those formations.

The last of the acidizing treatments is acid fracturing. Acid fracturing is the process of injecting high pressure fluids to break open the rock formation. The process is followed by injecting acid solution in order to etch the breaking surface. Etching the surfaces help in keeping a conductive path open even after the process is stopped when the fractures tend to close. The uneven surfaces created by acid etching leaves the fracture in the formation open which allows new conductive flow paths to form and allow the crude oil to flow from the formation into the well bore. The acid fracturing technique is normally used in tight reservoirs and mostly in carbonate formations [12].

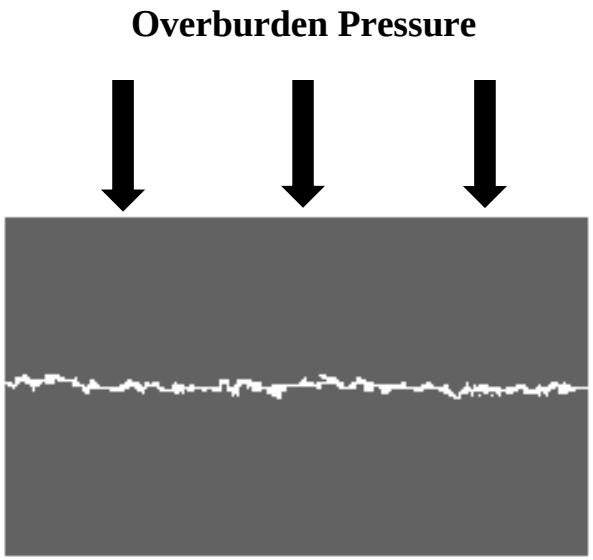

Figure 1: New conductive path was generated by acid etching

2.2 Chemistry of conventional acid solutions used for acidizing

Many acid mixture formulas were introduced to stimulate the reservoir. The most conventional chemical substance used in the field is the hydrochloric (HCl) based solution. Hydrochloric acid used in well treatment is commonly diluted to 15% and 28% concentration by weight [13]. It is economical, and has strong dissolution power. However, HCl has a tendency to cause asphaltic in crudes to precipitate in form of sludge or rigid layer. This by-product clogs pore space in a formation thus reducing the ability of crudes to flow in the treated zone after the treatment [14, 15]. A reaction of carbonate rocks with hydrochloric acid can be described as a chemical equation. An equation representing a reaction of limestone and hydrochloric acid can be showed as follows:

$$2HCl + CaCO_3 \leftrightarrow CaCl_2 + CO_2 + H_2O$$

Another example of the equation representing a reaction of dolomite and hydrochloric acid can be showed as:

$$CaMg\,(CO_3)_2 + 4HCl \leftrightarrow CaCl_2 + MgCl_2 + CO_2 + 2H_2O$$

Hydrochloric acid is a fast reaction acid; which means the acid reacts quickly at the surface of the reaction around the early path of the channel. The acid is spent quickly, thus preventing it from moving further into the reservoir formation. It results in relatively short wormholes, especially when the reservoir temperature is very high. A deeper reservoir, a long horizontal well, and/or an

open hole will all face the difficulty of controlling such a quick reaction rate of the hydrochloric based acidizing fluid [8, 16]. The fast reaction rate also limits the effective fracture length when used as acidizing fluid during acid fracturing [13].

Another class of acids that are commonly used for field treatment are organic acids. Organic acids have a slower reaction rate and lower dissolving power compared to hydrochloric acid. The slow reaction rate of organic acids help the acid solution penetrate deeper into the reservoir formation and create several wormholes instead of just enlarging the conductive path or being spent at the surface. The organic acid also has low corrosivity which alleviates the effect of corrosion on the field equipment. This is beneficial when the process requires long contact time between field equipment and acidizing solutions. Since the cost of the organic acid is higher than hydrochloric acid when comparing to the amount of calcium carbonate that can be dissolved, it is generally used as a mixture in acidizing fluids for field treatment. A commonly used organic acid in field treatment is acetic acid [8].

2.3 Previous study of the conventional acids used for acidizing and their alternatives

Acidizing techniques for well stimulation have always been developing to maximize oil production and reduce the damage that affects the equipment and environment during and after the process. Many acid types or combinations have been used for well acidizing. It is important to select a compatible acid solution or acid mixture, as well as carefully study the lithology of a formation for the well acidizing target, to maximize production and prevent damaging of a formation.

Hydrochloric acid is very acidic and have high dissolving power. Hence it is typically diluted to 15% by weight. It is also not uncommon to dilute it to 10%, 7% or even 5% to avoid precipitation

after well acidizing [13]. Hydrochloric acid would completely dissociate into H+ and Cl- ions. On the other hand, the degree of dissociation for organic acids is low and they do not separate completely under the reservoir conditions. Thus, organic acids will leave a portion of unspent volume after well treatment. One of the advantages of hydrochloric acid over organic acids is its ability to dissociate. This is mentioned in the work of Chang et al [17].

As the reactions progress, the amount of H^+ decreases, which elevates pH values in the formation. In addition, a formation which a pressure greater than 1000 psi will force carbon dioxide back into the solution [16]. Some of the carbon dioxide in the solution will stay in the form of carbonic acid. The carbonic acid acts as a buffer under the reservoir condition and can increase pH to 4.5. At this pH level, organic acid cannot dissociate completely [17]. This increase of pH in the formation greatly reduces the ability of organic acid to react with calcium carbonate because organic acid dissociates at a lower pH solution. For example, a study by Buijse et al. reported that in the final solution, which has a pH value of 5 and temperature of 200°F, only 54% of 10% acetic acid dissociates when equilibrium of the reaction is reached [18].

Another example of an incomplete reaction can be observed when another popular acid mixture for well acidizing is used. A mixture of 13% acetic acid and 9% formic acid, which has a dissolving power equivalent to 15% hydrochloric acid, is widely used in the industry. However, under the reservoir condition, because of effect of the products formed during and after the acid treatment, this acid mixture does not have the dissolving power of 15% hydrochloric acid. Instead, it has a dissolving power equivalent to 8% hydrochloric acid [18] . Table 1 shows the equivalent comparison of variety of acid mixture and HCl. The percentage spending of acids were calculated using the solubility product of calcium carbonate, the equilibrium constants of the reaction, and the acid dissociation constant to find the equilibrium pH. Then, the equilibrium pH is used in an

equilibrium reaction equation to find the quantity of un-dissociated acid as well as the percentage of acid spent [18]. The equations are listed in Appendix B.

Table 1: Equivalent comparison of acid mixture and HCl [18].

SPENDING OF ACID COMPONENTS IN ACID MIXTURES AND EQUIVALENT HCl CONCENTRATION				
	Acid Component Spent (%)			
Acid Mix	HCl	Acetic	Formic	Equivalent HCl (%)
10% acetic	—	54	—	3.4
10% formic	—	—	85	6.8
13/9% acetic/formic	—	31	82	8.5
7/11% HCl/formic	100	—	78	14.1
15/10% HCl/acetic	100	24	—	16.5

Organic acids have been used in the well stimulation of carbonate formations but, because of their complex reaction, potential precipitation and cost, organic acid is mostly used as a mixture in the acidizing fluid [17]. Even though the disadvantages of organic acids are inevitable, organic acids could perform better than hydrochloric acid in certain situations. Punnapala et al. studied the performance of 15% hydrochloric acid for well stimulation in the fields of the Abu Dhabi Company for Onshore Oil Operation. These unproductive wells were in a tight carbonate reservoir formation. The permeability of these fields was in the range of 0.6 to 80 mD. It was revealed in the study that the use of conventional acids, or 15% hydrochloric acid treatments, produced poor results after acidizing; only one third of 214 jobs produced positive results after treatment with 15% hydrochloric acid, especially in the zone that shows tight reservoir formation and that were completed with a long horizontal well. Punnapala et al. related Damkohler's number and diffusion coefficient to find an optimum flow rate which is required to create a wormhole after well acid stimulation. Due to the naturally fast reaction of hydrochloric acid and calcium carbonate, the

injection rate which would create a wormhole after acidizing in the tight formation and the long horizontal well would be so high that it is unrealistic for the pump to handle. Thus, a slower reaction rate acid or the addition of additives to slow the reaction, such as EDTA, HEDTA, weak acid, etc. would be viable options to use in these fields instead of hydrochloric acid [19] .

Using organic acids, such as acetic acid, formic acid, citric acid etc., as a weaker acid can slow down the reaction rates and result in a longer wormhole. In addition, it would reduce the corrosivity along the tubular and the equipment. However, another major drawback for using organic acid is precipitation after reaction. The products of reaction of the organic acid in the formation have also been a challenge to remove or prevent. As the study of Le Page at el. suggests, an insoluble salt is produced after the reaction of organic acids with calcium carbonate. Le Page et al. stated that when the concentration of organic or retard acid, such as acetic acid or formic acid, is more than the concentration at which calcium acetate or formate salts produced can be dissolved, these insoluble salts could be left in the formation reducing the permeability after the treatment. The maximum concentration of acetic acid and formic acid that could be used for well acidizing without leaving insoluble salts is 13 wt% and 9 wt% respectively [20].

One of the organic acids that can be used to prevent precipitation is citric acid. Citric acid is especially used in wells which have ferric (III). Ferric (III) in spent acid is less likely to dissolve, thus it precipitates in the form of ferric hydroxide. The addition of citric acid in the acidizing solution reduces the reaction rate, stabilizes iron and prevents precipitation during a well stimulation [21]. Even though, this prevents ferric hydroxide from precipitating, a study by Alkhaldi et al. shows chances of calcium nitrate precipitation when citric acid is used during well stimulation as an ion control agent, especially at high concentrations [22].

The composition of crude oil found in each reservoir determines the type of acid to be selected for well stimulation. Injection of hydrochloric acid for well treatment has a disadvantage that it can damage a formation that has asphaltenes in the crude oil. Moore et al.'s study on the Swan Hill formation showed that sludge and film emulsions are formed when crude oil comes in contact with hydrochloric acid at all concentrations above 1%. The test on the Swan Hill formation showed that sludge was formed quickly and the amount of sludge increased as the time of contact increased. [14] Another significant loss of permeability after well treatment can result from the reaction of hydrochloric acid with aluminosilicate minerals. This reaction produces particles that can impede the fluid from migrating through the channel. The work of Bryant et al. shows a permeability reduction of 35% when coreflood testing was conducted on core samples containing aluminosilicate minerals [23].

Conventional acids used for acidizing also met with difficulties in controlling fluid loss during matrix acidizing and acid fracturing. Buijse's work which analyzes wormhole mechanism by numerical calculations show that more than 90% of the fluid is lost along the fluid path i.e. only a very small amount of unspent hydrochloric acid reaches the end of the wormhole. This loss minimizes the length of the wormhole. Fluid loss is a very important parameter for selecting acid solution when designing an acid fracturing treatment. Hydrochloric acid lost along the fracture minimizes the etching length for acid fracturing resulting in poor conductivity [24].

2.4 Corrosion of the field equipment

Corrosion during well stimulation can be mainly attributed to the steel or iron pipe being in constant contact with an acid stimulation fluid. It has been a problem for the oil industry, specifically when hydrochloric acid is used in high concentrations or when used without a

corrosion inhibitor. Hydrochloric acid has a tendency to break down iron due to the strong reaction between the chloride ion and the base metal. The reaction dissolves metal and produces hydrated iron oxide. This event, commonly called corrosion, creates one of the major problems in the oil production field because it damages the equipment and increases the cost of production dramatically. To minimize the corrosion effect during the process of well stimulation, corrosion inhibitors are introduced to alleviate the reaction of hydrochloric acid to the steel or iron equipment. However, they are hazardous to the environment due to the high level of toxicity. Some corrosion inhibitors can be extremely toxic to not only the environment but also human health [25]. There are demands to limit or replace using toxic compound in corrosion inhibitor during well acidizing. One of them is The Convention for the Protection of the Marine Environment of the North-East Atlantic or OSPAR Convention which is representing 15 countries in the western coast Europe and the European Union has a goal to limit all discharge chemical that can be toxic to environment by 2020 [26].

In addition, the reaction between hydrochloric acid and equipment or tubular could unintentionally reduce the permeability of the reservoir. The permeability after well treatment could be affected by the presence of Fe (II) and/or Fe (III) in the formation or by the introduction of Fe (II) and/or Fe (III) into the formation. This introduction occurs when conventional acid reacts with coils, tubing, etc., and rusted parts of the equipment. An iron ion that is generated after reaction is washed down to the formation during the treatment. This event contaminates the acidizing solution and increases the amount of Fe (II) and/or Fe (III) in the formation. Iron in the crude oil could precipitate after well acidizing. This is because the iron dissolves during reaction but precipitates after the acid is spent and the pH in the reservoir is raised. Fe (III) and hydroxide can form a sludge when pH is above 1 [21] and the presence of hydrogen sulfide can result in the formation of a

sludge with Fe (II) when the pH is more than 6. In addition, a reservoir with high temperature would decrease the solubility of iron in the crude oil, thus escalating the chance of sludge in the formation. This precipitation reduces the performance of the treatment by clogging the formation and preventing oil from flowing to the wellbore. In some cases, the formation could be shut off, requiring a lot of time and re-investing to bring the reservoir back to its previous condition. Sludge formation or emulsification depends on many factors, but iron containing minerals in the reservoir and the introduction of Fe (II) and/or Fe (III) from tubing or equipment is quite a significant factor. Anti-sludge additives have been applied to prevent this problem. It can reduce the size of the sludge formed but it is very difficult to completely prevent the sludge from forming. Moreover, the anti-sludge additive could cause the reverse emulsion and increase a capital cost for well treatment. Thus, based on downhole conditions, only an appropriate iron stabilizing agent can prevent the sludge from forming at reservoir conditions. Therefore, a careful study is needed for well acidizing design [14, 21, 27]. Corrosion inhibitors is commonly added to the treatment fluid to prevent the corrosion, nonetheless the cost of these product is high and subsequently increase the production cost.

2.5 Environmental impact of the acidizing solution

Hydrochloric acid is the most commonly used acid used for well stimulation. It is very unsafe to human health and the environment. The reference concentration, which is estimated to be a point where continuous inhalation is unlikely to have a negative impact on human health, is advised not to exceed 0.02 milligrams per cubic meter or 0.000076 milligrams per gallon. However, this study is based on effects in rats [28]. The material safety data sheet (MSDS) rates hydrochloric acid as 3 out of 4 for danger to human health. Hydrochloric acid can be fatal or causes circulatory to fail

when humans or animals ingest or inhale it. It causes severe irritation for eyes and skin in humans and death to aquatic life when come into contact with it. Furthermore, hydrochloric acid can have a negative impact during child development [29, 30]. The MD guidelines which has an extensive medical and health related information is recommended amount that human can be exposed to is 10 parts per million. The concentration of 35 parts per million would irritate the throat and 1300 to 2000 parts per million can cause death [31]. Even more, the Occupation Safety and Health Administration of United States Department of Labor (OSHA) set the Permissible Exposure Limit or PEL for a general industry at 5 parts per million [32]. Additionally, The List of MAK and BAT Values which advocates for a safety workplace set the maximum concentration of HCl in the work area at only 2 parts per million [33]. In 2013 the records from the American Association of Poison Control Centers Toxic Exposure Surveillance System show 1923 cases related to hydrochloric acid. Fifteen people had severe health concerns and two deaths were caused by exposure to hydrochloric acid [1].

Hydrochloric acid is not the only chemical used as an acidizing fluid. To slow the reaction of the hydrochloric acid, to reduce the corrosion during the process, to prevent precipitation and to optimize the acidizing process, additional chemicals have to be added. These additives are critical for the well stimulation process but they are costly and most importantly, harmful to the environment and human health. These chemicals in acidizing fluids used in well stimulation can cause many risks to the environment and worker health during and after the process.

Well treatment with the conventional acids become a major concern to our society. Many cities are advocating and regulating the rules to ban the well acidizing because of a potential health effect on human, water sources and environment causes by acids left after the well treatment [34, 35, 36, 37]. Abdullah et al. reported that more than 600 acidizing jobs were performed in the southern and

central part of urban areas in California between April 2013 and August 2015 [3]. The jobs required more than 200 different chemicals. Out of 200 chemicals, 90 had a nonspecific name or unidentified amount and 28 have been rated F, which is the lowest grade a chemical can receive from the Quick Chemical Assessment Tool or QCAT.

The QCAT is a tool created by the Washington State Department of Ecology that uses a chemical endpoint to evaluate and grade a chemical for toxicity [38]. The QCAT gives a chemical a grade between A and F where A represents the safest chemical and F is the one that should be avoided. The F grade chemicals are sources of concern for carcinogenicity, mutagenicity & genotoxicity, reproductive toxicity, developmental toxicity, or endocrine activity in humans. In addition, F graded chemicals also cause acute aquatic toxicity and acute mammalian toxicity.

2.6 The Ultra Series FF-01

The Ultra Series FF-01 is the new chemical compound for future well treatments. It was created and developed by EARTHBORN CLEAN, a division of Earthborn Environmental Technologies, LP. The company is based in the state of Kansas (USA). The Ultra Series FF-01 is very acidic (pH less than 1), has a slow reaction rates and can work up to 72 times longer than hydrochloric acid. It is biodegradable, experimentally proven to have the potential to increase productivity and is non-corrosive to the field equipment [39]. The Ultra Series FF-01 has also been tested and proven not to create emulsification with Lansing Kansas City and Mississippian crude oil. Apart from all these advantages, this acidizing fluid is also environmentally friendly. The Ultra Series FF-01 has minimum effect on human health and marine life. It received grade letter A, from the QCAT.

Markey et al. studied the properties of the Ultra Series FF-01, especially its ability to dissolve carbonate rocks and to generate wormholes [39]. The rheology of Ultra Series FF-01 (Figure 2),

when studied with an Anton Paar rheometer, showed that it is shear thinning and has higher viscosity when compared to hydrochloric acid. Both of these properties are favorable during the well stimulation process because they reduce leak off, especially when the Ultra Series FF-01 is away from the well bore where the shear rate is minimum.

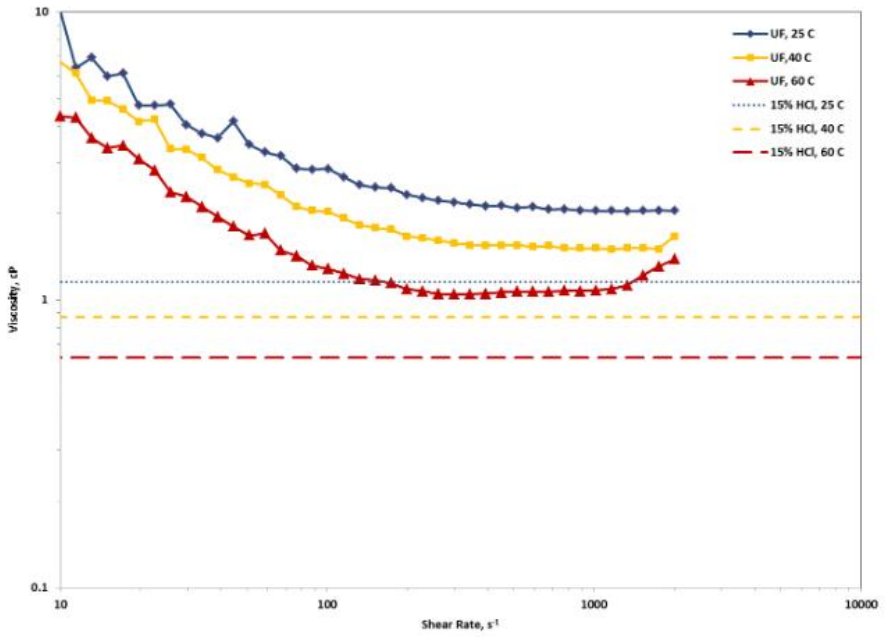

Figure 2: Viscosity comparison between the Ultra Series FF-01 and 15% hydrochloric acid, after Markey et al [39].

The solubility of carbonate rocks in Ultra Series FF-01 was tested with a beaker test. Results show that Ultra Series FF-01 has a slower rate of reaction compared to hydrochloric acid and it took two hours more to complete the reaction. In addition, the residue left after carbonate rock reacted with the Ultra Series FF-01, was significantly lower compared to the residue left after reaction with 15% hydrochloric acid for the same period of time. This means that chances of residue clogging

or blocking flow path is lower when Ultra Series FF-01 is used. Figure 3 shows the plot of calcium concentration with time during the beaker test.

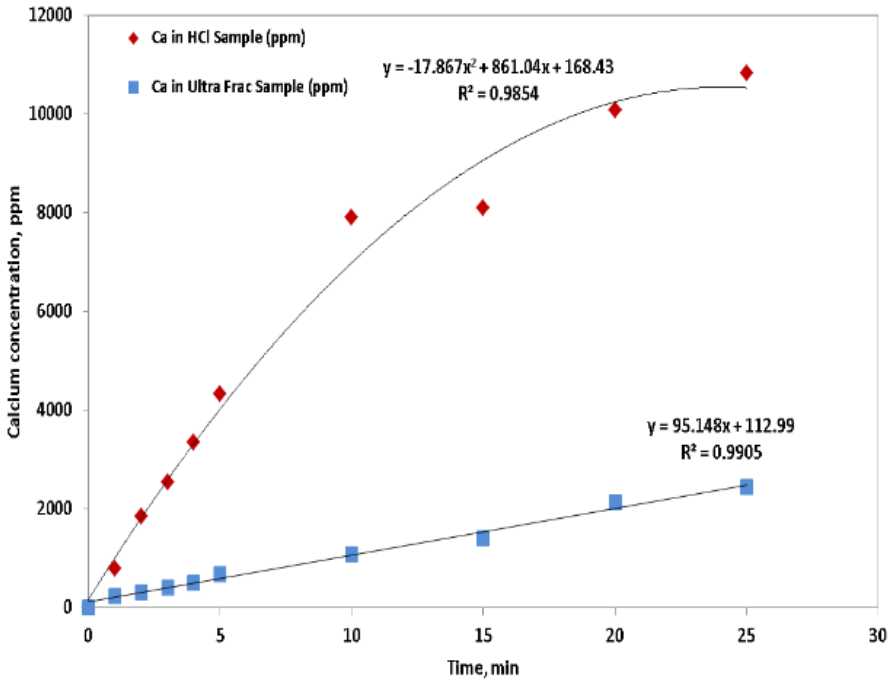

Figure 3: Calcium concentration vs time, after Markey et al. [39]

3. Materials

All of the chemicals and crude oil used in this experiment are shown in this section. This section also describes a preparation for the chemical used during matrix acidizing and acid fracturing experiment. In addition, this section describes characteristic, shapes and dimension of cores and rods used for this research.

3.1 Commercial acidizing fluids

Hydrochloric acid (HCl) is used as a base chemical for an acidizing fluid. To replicate a commercial acidizing fluid, HCl was diluted to 15% concentration by weight by mixing it with deionized and reverse osmosis water. The preparation for diluted 15% HCl were done under the fume hood to prevent any hazardous vapor mixture escaping into the laboratory. Additives like iron control, non-emulsifier, corrosion inhibitor, and micro emulsion surfactant were added to the diluted solution of HCl. The concentration of the additives used in the 15% HCl are 3 ppm of The Reducer^{TM} iron control additive (Chemplex Advanced Materials), 2 ppm of Plexbreak-150 M non-emulsifier additive (Chemplex Advanced Materials), 2 ppm of CRONOX^{TM} AK-50 corrosion inhibitor additive (Baker Hughes) and 1 ppm for Plexsurf 285 micro-emulsion surfactant (Chemplex Advanced Materials). The stirring rate for the preparation was 500 rpm. HCl was purchased from Fisher Scientific. The lot number of HCl was 085025 and its CAS number was 7647-01-0. The additives were made available by 101st Earthborn Environmental Technologies, LP.

3.2 The Ultra Series FF-01

The Ultra Series FF-01 was provided by 101st Earthborn Environmental Technologies, LP. In most cases, it was used without any dilutions nor were additives needed. However, to study a possibility to use low concentration of the Ultra Series FF-01 during matrix acidizing, the products were diluted to 50%, 75%, and 90% by weight. The dilution was done by mixing it with deionized and reverse osmosis water. The Ultra Series FF-01 also was mixed with 15% HCl to study the performance of this blend to generate wormhole and increase permeability. The ratio of the Ultra Series FF-01 and 15% HCl mixtures were 1 to 1, 2 to 1, and 3 to 1.

3.3 Acetic acid

Acetic acid is an organic acid that was used during matrix acidizing experiment to compare its ability to increase core permeability with that of the Ultra Series FF-01. The acetic acid for this experiment was diluted to 10% by weight. The diluted acetic acid was prepared with the stirrer at 500 rpm under the fume hood. Acetic acid was purchased from Fisher Scientific (Hampton, NH). The lot number for acetic acid was 123977 and its CAS number was 7732-18-5.

3.4 Brine

This experiment used 2% wt potassium chloride (KCl) as brine. It was prepared by mixing KCl with deionized and reverse osmosis water in a container and stirring them on the stirrer at 700 rpm for at least five hours. The containers were closed to prevent evaporation. The KCl was purchased from VWR. Its CAS number was 7447-40-7 and the lot number was 1015C371. The viscosity of 2% wt KCl was 0.95 cP at 25 °C.

3.5 Mississippi crude oil

Mississippi crude oil is one of the crude oil samples that was used to test the viscosity at the layer between crude oil and the acidizing fluid. The viscosity of the Mississippi crude oil at 40 °C is shown in Figure 4 at different shear rate.

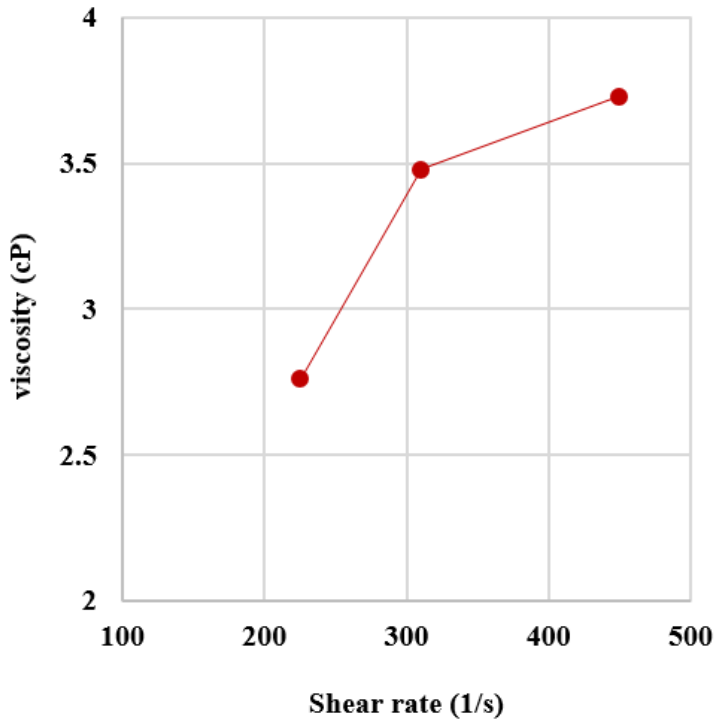

Figure 4: Viscosity of the oil-acid sludge made by the Mississippi crude oil, vs shear rate.

3.6 Lansing Kansas City crude oil

Lansing Kansas City oil was another crude oil that was used to test the viscosity at the interface of the crude oil and acidic sample solution. The viscosity of Lansing Kansas City crude oil versus shear rate at the temperature of 40 °C is shown in Figure 5.

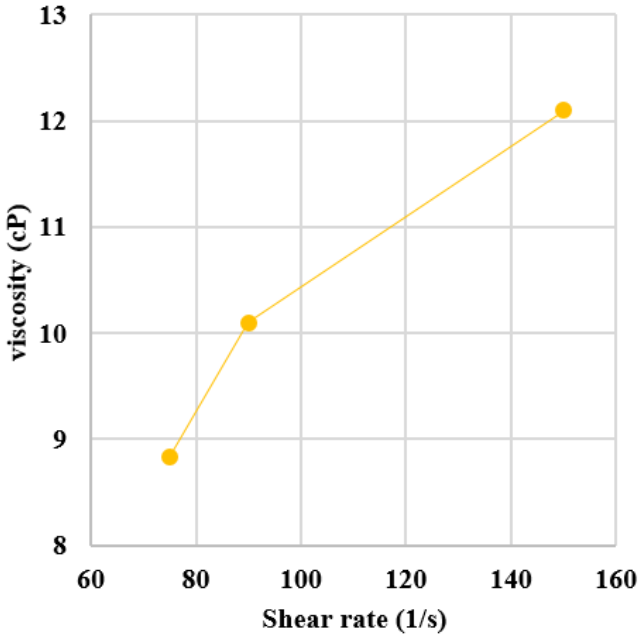

Figure 5: Viscosity of the oil-acid sludge made by the Lansing Kansas City crude oil vs shear rate.

3.7 Core samples

The core samples used for the experiment are carbonate rocks. However, there are two types of core samples. One of the core samples used for matrix acidizing is Indiana limestone. They are cylindrical in shape. These cores had a diameter of one and a half inch and were cut into three inches in length. The core sample of Indiana limestone and its dimension can be seen in Figure 6 and Figure 7 respectively. The permeability is in the range of 0.5 to 350 mD. The porosity is 10-15%.

Figure 6: A dry Indiana limestone core plug.

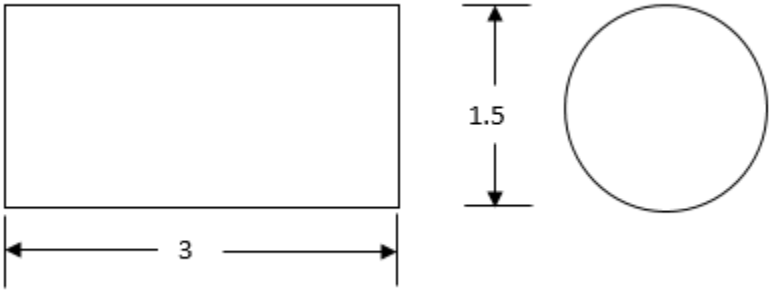

Figure 7: Indiana limestone core plug dimensions

Another type of core which was used for acid fracturing were 1.425” x 6.8” x 1.5” Lueders limestone core wafers. The permeability for these cores is in the 0.5-1.5 mD range and their porosity values are within the 5-7% range. They are sealed on the side with silicon by using a block mold before the conductivity experiment. The company which provided the core samples was Kocurek Industries Inc. Figure 8 is the Lueders limestone core wafers with the silicone on their side. The measurement of the Lueders limestone is shown in Figure 9.

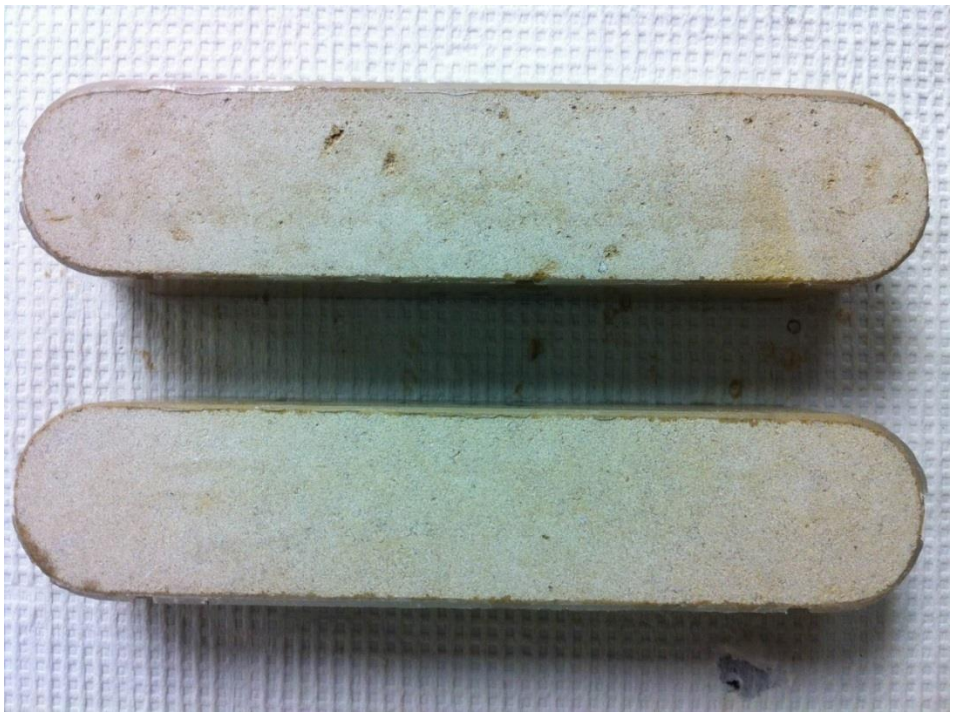

Figure 8: Lueders limestone core wafers were sealed on the side by silicon for acid fracturing experiment.

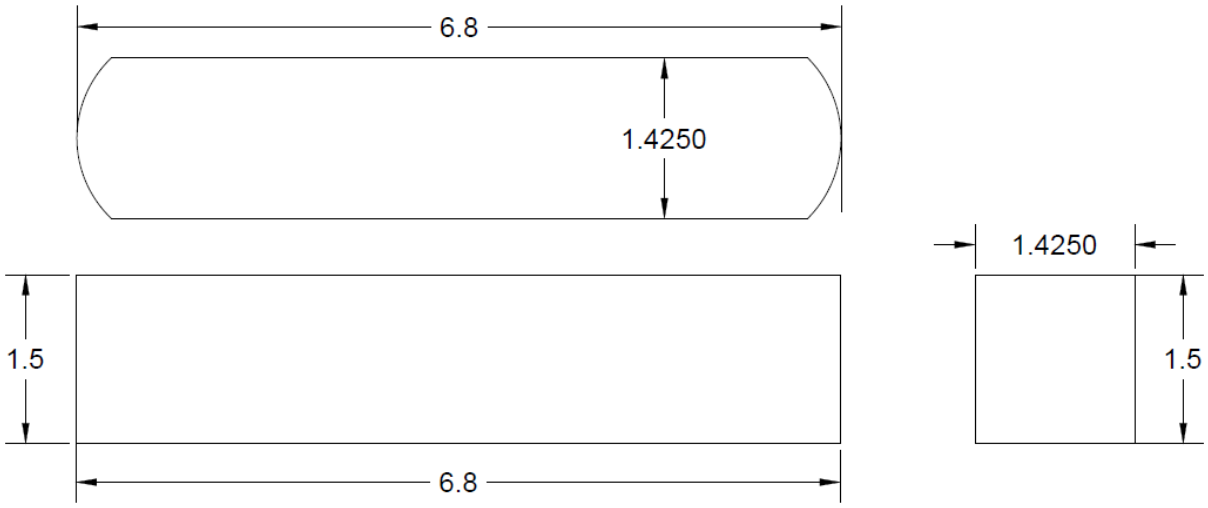

Figure 9: Lueders limestone core plug dimensions

3.2.2 Stainless steel plates

Two stainless steel 316 plates which were exactly off the same size and dimension were used for corrosion testing. The stainless steel rods' dimensions were 3 inches in length, 1.5 inches in width, and 0.046 inches in thickness.

4. Experimental procedures

This section introduces and explains step by step procedures for all of the experiments used during this research. It also includes equipment diagrams for matrix acidizing test and acid conductivity measurement. The experimental procedures in this research are beaker testing for corrosion, beaker testing for rate of reaction, beaker testing for emulsion, interfacial tension measurement, viscosity

testing by using Brookfield viscometer, core saturation, matrix acidizing tests with coreflooding, and acid conductivity measurements.

4.1 Beaker testing for corrosion

The beaker testing was done to study the effect of acidic sample solution on stainless steel material. To determine the effect on stainless steel, two stainless steel plates were cut into the same shape and size. They were weighed to get an initial weight. The procedure proceeded by preparing a 200 mL sample of the 2% KCl in Ultra Series FF-01 in the beaker, a 200 mL sample of 2% KCl in 15% HCl in another beaker and a 200 mL sample of 15% HCl with field's additive in the last beaker at 40° C. Then, the stainless steel plates were placed into each beaker. The beakers which contained stainless steel plates and the sample of the 2% KCl in Ultra Series FF-01, 2% KCl in 15% HCl and 15% HCl with additives were left at the 40° C under the fume hood for 24 hours. The stainless steel plates were removed from the beaker after the first hour and the excess acidic solution around the stainless steel rod was wiped off. The stainless steels were left to dry. Then, the stainless steel rods were measured to get the final weight. Again, the stainless steel plates were removed from the beaker and weighed after second, fourth, sixth, ninth, twelfth, sixteenth, twentieth, and twenty forth hour.

4.2 Beaker testing for rate of reaction

The rate of reaction of the Ultra Series FF-01was compared with 15% HCl using calcium carbonate powder by beaker testing. To compare the rate of reaction on calcium carbonate powder, the experiment starts with preparation of a 300 mL of the Ultra Series FF-01 in the beaker at room condition. Once the Ultra Series FF-01 is ready, carefully add the calcium carbonate powder into

the beaker. As soon as the calcium carbonate powder is completely dissolved, record the time and add more calcium carbonate powder into the beaker. Keep adding the calcium carbonate powder and record the time until the calcium carbonate powder is not dissolved in the Ultra Series FF-01. Repeat the experiment with 15% HCl.

4.3 Beaker testing for emulsion

In some cases, the acid used in well acidizing causes a stable emulsion which reduces the ability of oil to flow and creates complex problems in the formation. So emulsion test for the Ultra Series FF-01 with Lansing Kansas City was conducted. To test a formation of emulsion, a 50 mL of Lansing Kansas City crude oil is added into the container. Then, another 50 mL of the Ultra Series FF-01 is added into the same container. Close a lid container and shake well. Place the container in the oven at 40° C. Take a picture every two hours for the first eight hours, then at twelfth and twentieth hour. Repeat the procedure with 15% HCl and the Lansing Kansas City crude oil. Again, repeat the procedure with 15% HCl with additives and the Lansing Kansas City crude oil.

4.4 Interfacial tension measurement

It will be very beneficial to know the interfacial tension value of the Ultra Series FF-01 and the Lansing Kansas City crude oil for well acidizing. Thus, the interfacial tension (IFT) experiment was performed for different concentration of the Ultra Series FF-01 in the 2% KCl and the Lansing Kansas City crude oil at the temperature of 40° C. The procedure of IFT measurement is as followed:

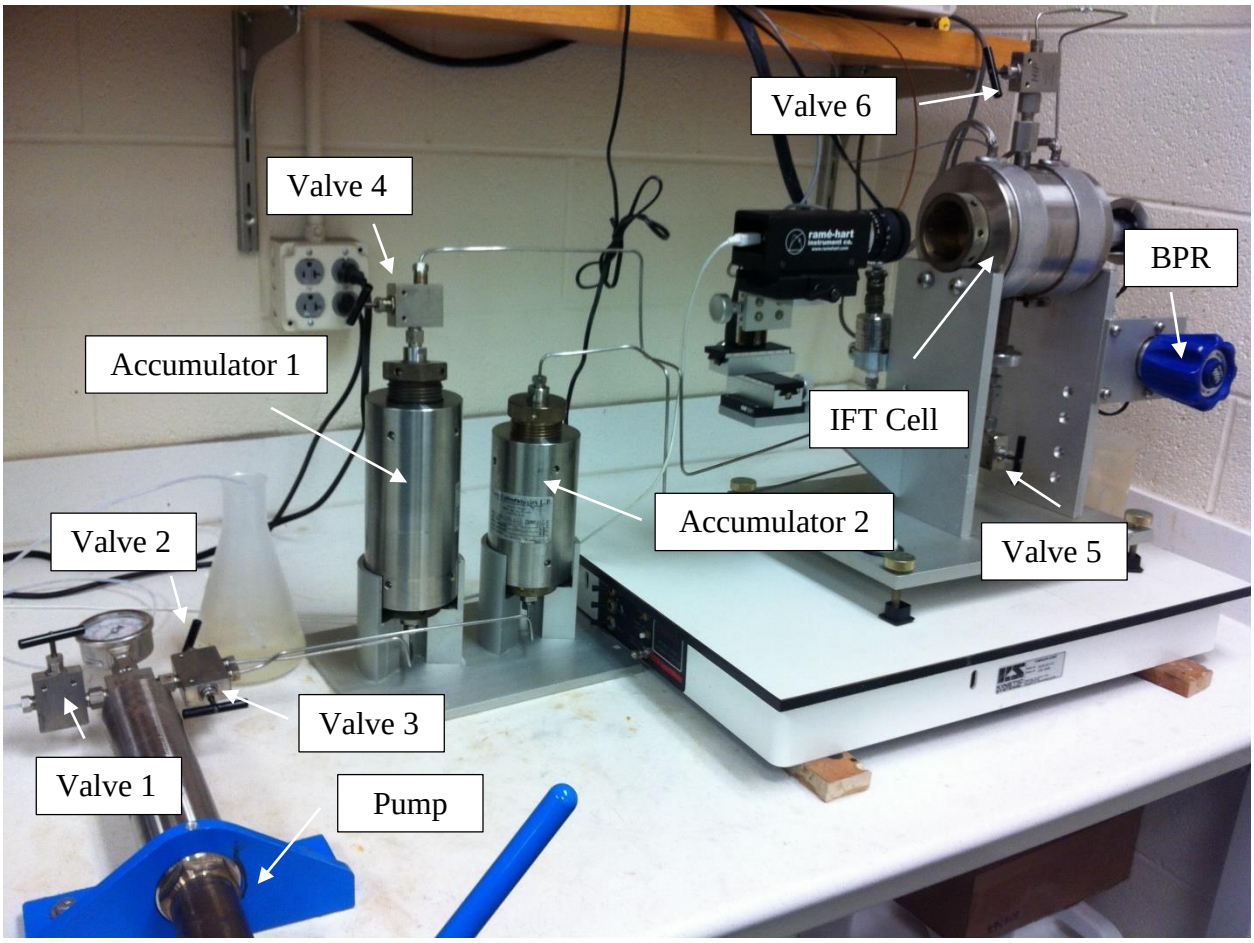

Figure 10: Interfacial tension measurement setup.

1. Open valve 1.
2. Close valve 2 and 3.
3. Fill a pump with reverse osmosis water by turning a pump handle counter clockwise.
4. Close valve 1.
5. Fill accumulator 1 with the Ultra Series FF-01 and close the lid of accumulator.
6. Open valve 4 and 6.
7. Fill accumulator 2 with the Lansing Kansas City crude oil and close the lid of the accumulator.
8. Turn the back pressure regulator knob fully counter clockwise

9. Close valve 3 and valve 5.
10. Fill the IFT cell with the Ultra series FF-01 by turning the pump handle clockwise.
11. Turn the heater on to 40° C
12. Once the temperature is 40° C, close valve 2 and 6.
13. Open valve 3.
14. Increase the pressure in the pump and the accumulator 2 by turning the pump handle clockwise.
15. Slowly open valve 5 to create a sample droplet in the IFT cell.
16. Use the Rame-Hart software to record the measurement and take a picture.
17. Repeat step 15 and 16 for four different size of droplet.
18. Repeat the procedure with 50% Ultra Series FF-01: 50% of 2% KCl in accumulator 1.
19. Again with 10% Ultra Series FF-01: 90% of 2% KCl in accumulator 1.
20. Finally, repeat the procedure with only 2% KCl in accumulator 1.
21. Finally, repeat the procedure of 50% Ultra Series FF-01: 50% of 2% KCl in accumulator 1 and 10% Ultra Series FF-01: 90% of 2% KCl in accumulator 1 when the pressure in the IFT cell is increased to 500 psig.

4.5 Viscosity testing by using Brookfield viscometer

The procedure to measure the viscosity of the crude oil sample after they come in contact with acidic sample solutions are as following (the crude oil samples used in this experiment were Lansing Kansas City and Mississippi limestone crude oil samples).

1. A 50 mL Lansing Kansas City crude oil sample was prepared in a container.
2. A sample volume of 50 mL of Ultra Series FF-01 was added into the same container.

3. Then, close and shake the container very well.
4. After the sample solutions are mixed well in the container, place the container in the oven at 40° C for 24 hours.
5. After 24 hours, collect the sample of the Kansas City crude oil at the interface with the Ultra Series FF-01 using a syringe.
6. Turn on the Brookfield viscometer and set the temperature to 40° C.
7. Allow the Brookfield viscometer to reach the targeted temperature.
8. Once the temperature of 40° C was reached, place the collected sample into the cup collector.
9. Turn the viscometer on and hit set speed.
10. Press the up arrow to start rotating the disk.
11. Leave the viscometer until the number indicating the value of viscosity is stable. If the viscosity number is not stable, increase the speed of the rotating disk or shear rate by pressing the up arrow.
12. Obtain three viscosity values by increasing the shear rate.
13. Repeat the procedure with 15% HCl.
14. Next, repeat the procedure with 15% HCl and all of its additives.
15. The same procedure was repeated for the Mississippian limestone crude oil, first with the Ultra Series FF-01, followed by 15% HCl alone and finally with 15% HCl and all its additives.

The Brookfield viscometer before the experiment are shown in the Figure 11.

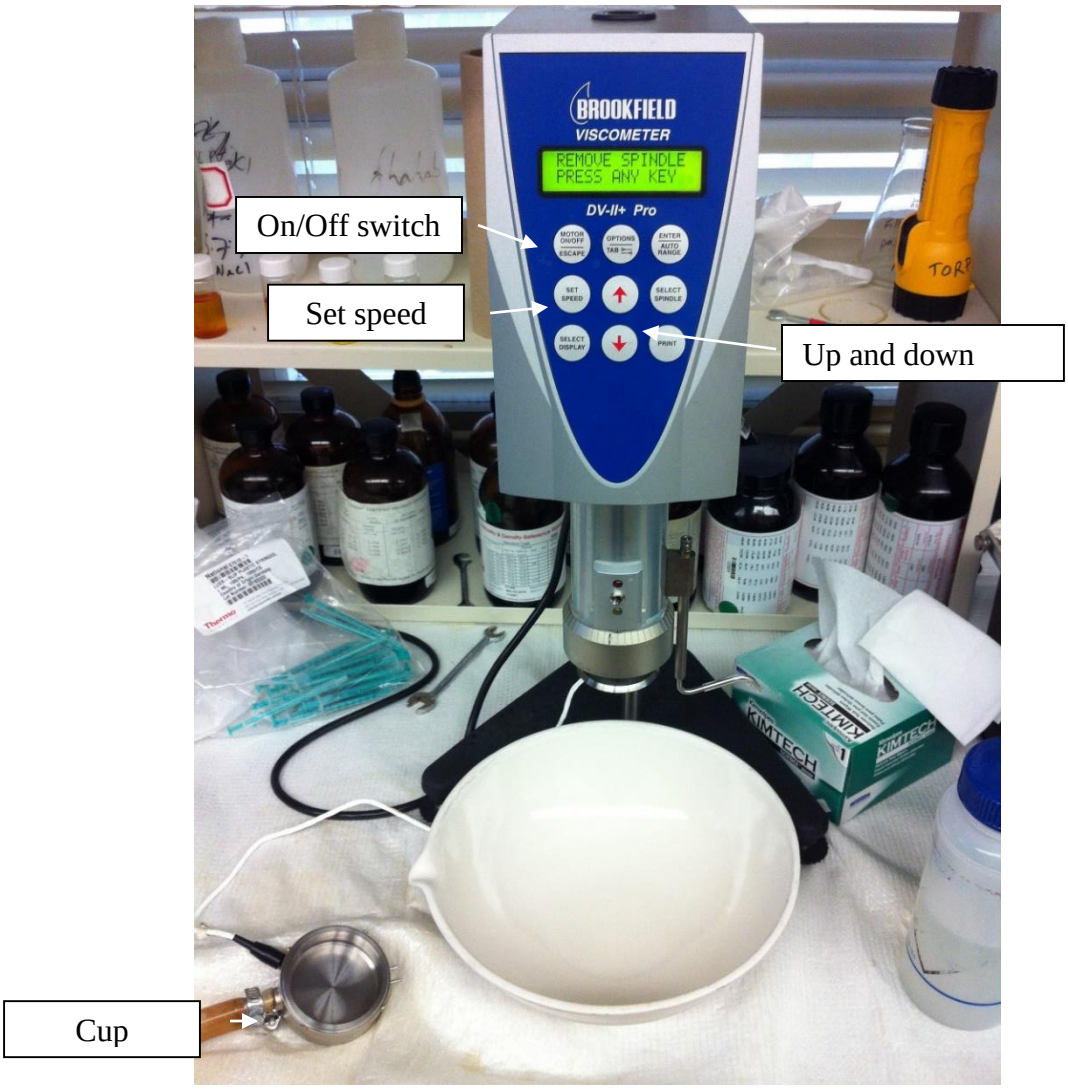

Figure 11: Brookfield viscometer with a cup collector in the bottom left corner.

4.6 Core saturation

In order to mimic the reservoir conditions, the core sample will be fully saturated with brine sample through a core saturation process. The process starts with inserting the core sample into a seal container. Then, any air inside the core sample is removed by using a vacuum pump. After all air is removed, 2% KCl is allowed to enter and fill the pores. The procedure for the core saturation is listed below and Figure 12 shows different parts of the system.

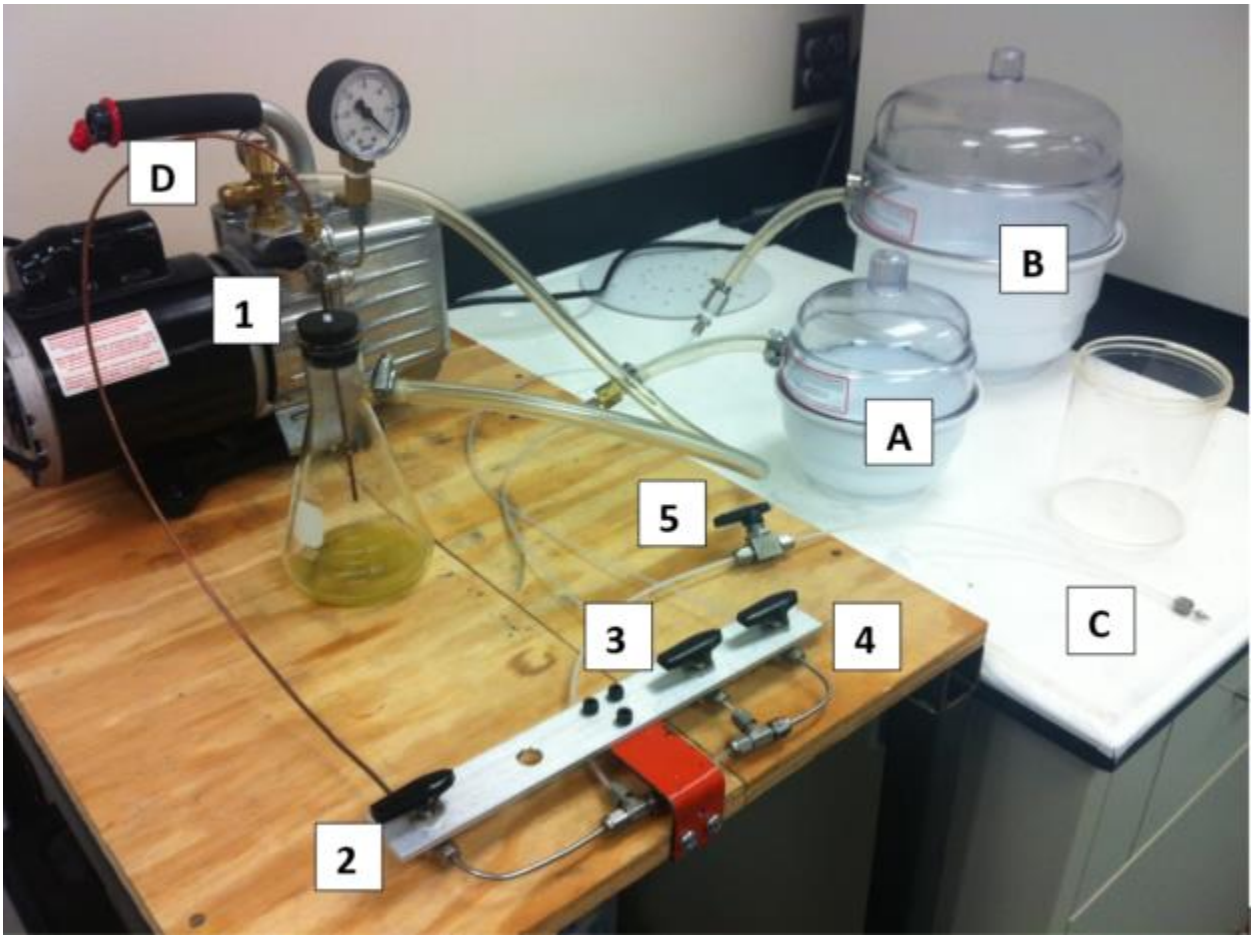

Figure 12: Core saturation set up

1. Prepare 2% KCl in the in a beaker
2. Measure core dimensions
3. Weigh the sample dry core
4. Place the sample core in container (A or B)

   *For this procedure we selected the container A
5. Open valve 2 and 3 (turn the valve in line direction)
6. Close valve 4 and 5 (turn valve in perpendicular direction to the line)
7. Open valve 1

8. Start the pump
9. Wait for 35 minutes till the gauge pressure reads -25 PSI or lower
10. Close valve 1
11. Turn off the pump
12. Close valve 2
13. Fill line C with the 2% KCl
14. Carefully place the end of line C in the sample solution container so there is no air in the line
15. Open valve 5
16. Let the 2% KCl fill the container until the core sample is completely submerged with the sample solution
17. Close valve 5
18. Leave the core sample for 15 minutes
19. Open valve D to release pressure in the system
20. Close valve D
21. Take the core sample out and quickly remove excess water
22. Weigh the wetted core sample
23. Subtract wetted weight with dry weight and divide it by density to get pore volume
24. Calculate the pore volume over bulk volume fraction as the porosity of the rock sample

4.7 Matrix acidizing procedure

Coreflood setup has been widely used for simulation of the matrix acidizing process in the laboratory. It provides a way to study the ability of the acidizing sample fluid to generate

wormholes, and to examine the core sample after it comes to contact with the acid. The setup can be used to study the influence of temperature, injection rate, and back pressure for a well acidizing process. In addition, the effect of the injection fluid can be studied by the use of the core flood setup [39, 40]. The major components of the setup are a core holder, an accumulator, an injection pump, a back pressure regulator, an overburden pressure pump, a pressure transmitter and a heater. The setup mimics the reservoir pressure and temperature. It allows injections while maintaining the pressure of the system. This ability replicates the well stimulation process in the field. Additionally, the core flood setup can be used to measure the core permeability. Thus the setup is an ideal tool to first perform the matrix acidizing and then to find the increase in permeability of the rock sample. The process of matrix acidizing by using the core flood setup starts with inserting a core sample inside the core holder and applying overburden pressure. The next step is to inject a brine and follow it with acidizing fluids. Finally, the brine is injected once more to clean up the process and measure the final permeability created by the acidizing fluids. The permeability is calculated by using the Darcy's law.

$$k = -\frac{q\mu L}{A\Delta P} \qquad \text{Equation 1}$$

Where:

A	=	Cross sectional area (cm^2)
k	=	Permeability (D)
L	=	Length (cm)
ΔP	=	Pressure difference (atm)
q	=	Flow rate (mL/s)
μ	=	Viscosity (cp)

The core flooding setup for this research is a modified version of the previous core flooding setup that were using in the Unconventional Resources Laboratory at the University of Kansas. This setup was used for conducting the linear matrix acidizing experiment and studied variety of conditions that can influence the outcome of the matrix acidizing (e.g., injection rate, temperature, back pressure, or acidic sample solution). The setup was designed to handle the pressure in the line up to 2500 psi. The purpose of this design was to ensure that CO_2 produced from the reaction during matrix acidizing remained in the solution thus ensuring a single phase flow system. The main objective of this experiment was to compare the increased permeability factor caused by injecting different acidic sample solutions through the Indiana limestone or reservoir core samples at various conditions.

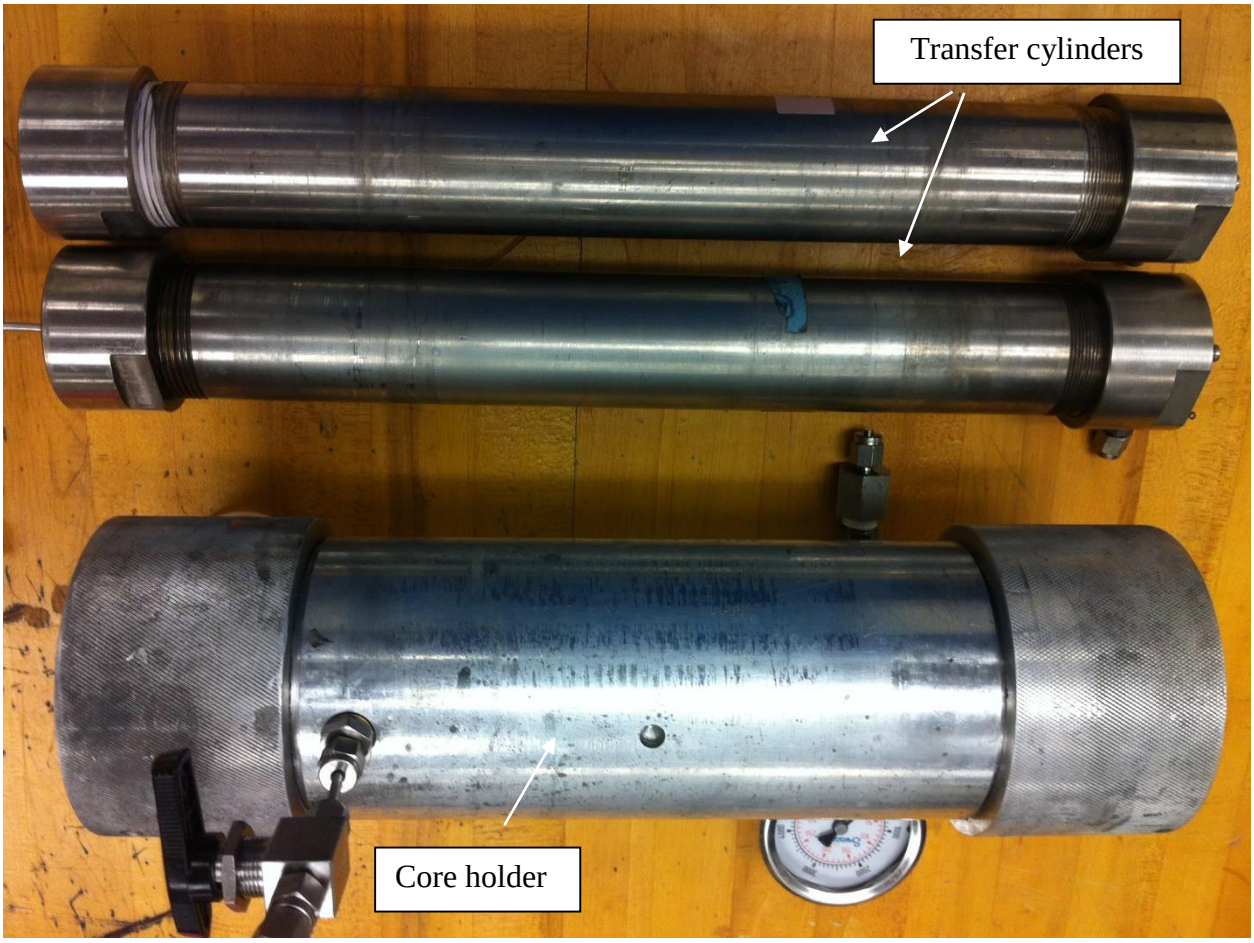

Figure 13: Transfer cylinders (Top) and the core holder (Bottom) used for matrix acidizing experiments.

A core holder and transfer cylinder are shown in the Figure 13. The core holder was made of stainless steel with a Viton sleeve inside. The Viton sleeve provides a grip to the side of the core sample to prevent the injected solution from bypassing the core material while the system is injecting. The core holder requires 1.5 -inch core diameter but can be 2 – to5 -inch long. In this experiment, we used 3-inch cores. The core holder is connected with transfer cylinders. These transfer cylinders contain sample solutions which are injected into the core holder by a Teledyne ISCO pump during the injection period. A back pressure regulator was used to control the overall pressure. The setup is connected to a pressure transducer to record the pressure differential across

the core sample by a LabVIEW program. Figure 14 shows the core flooding setup during the experiment and Figure 15 is schematic of the core-flooding setup.

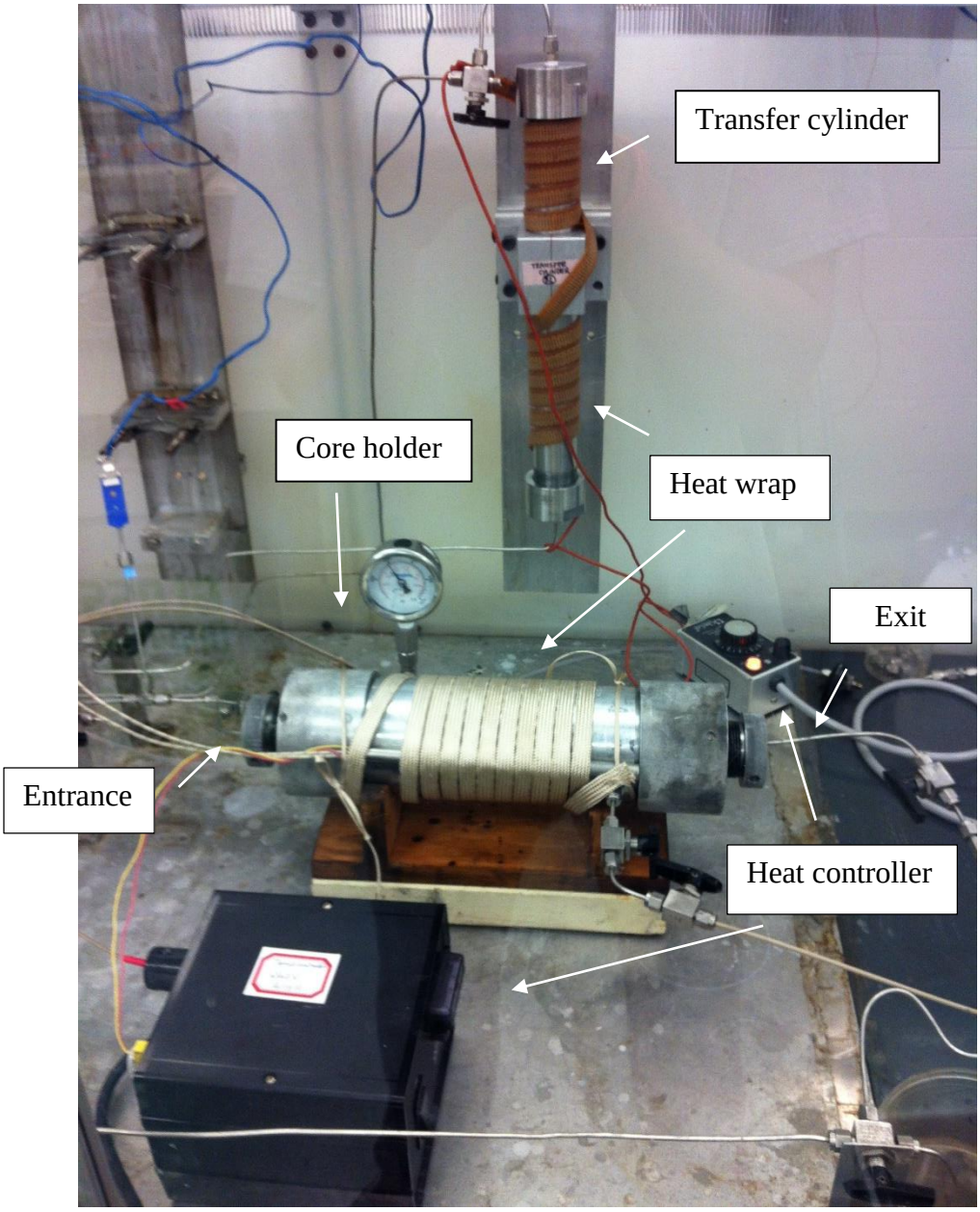

Figure 14: Core-flooding set up during the experiment.

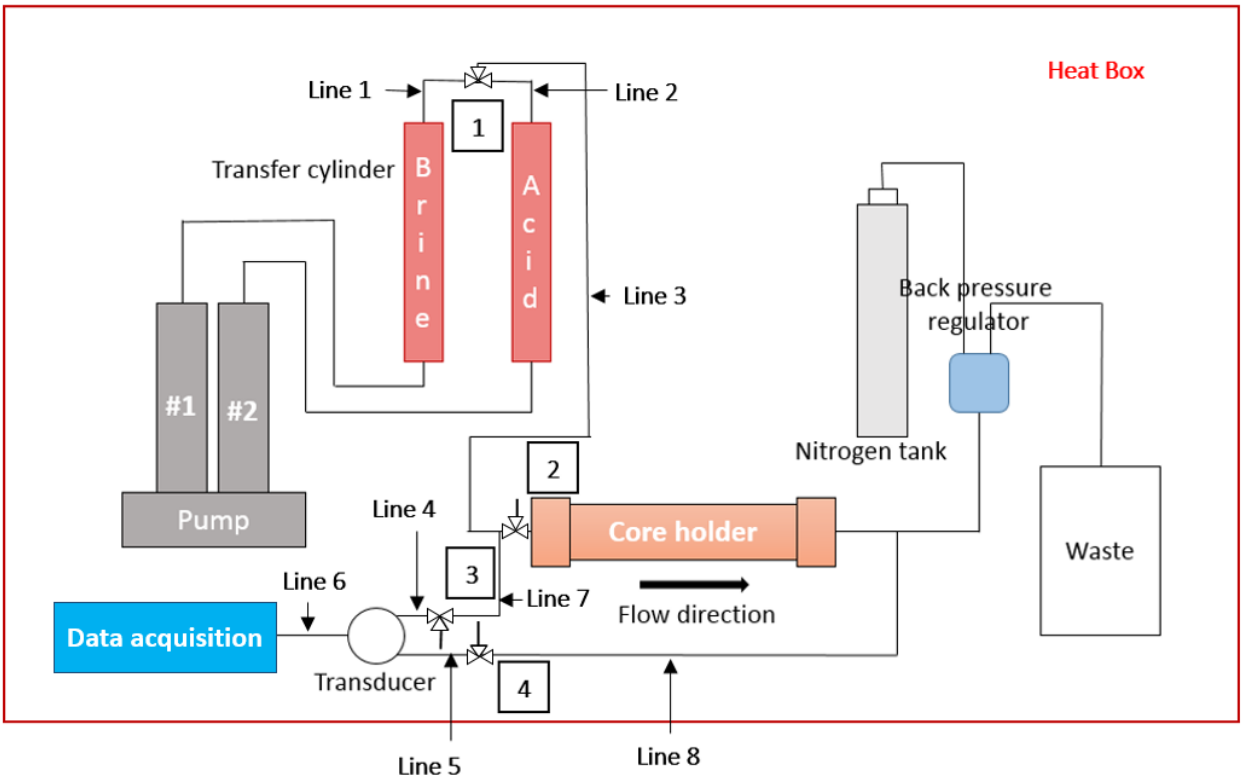

Figure 15: The schematic of the core-flooding setup

Using the saturated core samples discussed in the previous section, the following steps were followed for the matrix acidizing experiment.

1. Fill a transducer and transducer lines (4, 5, and 6) with mineral oil.
2. Prepare 2% KCl and fill the transfer cylinders with that
3. Prepare the acidic fluid sample and fill the second transfer cylinder
4. Turn the heater on and set the temperature to the targeted temperature.
5. Allow the sample fluid and the system to reach the targeted temperature.
6. Place the core sample in the core holder
7. Connect line 1 and line 3 by switching valve 1
8. Inject brine through the system and wait until there is brine at the exit

9. Switch the valve 3 open to the outside of the system to remove any air in the line
10. Once there is no air in the line, switch valve 3 to connect line 7 with line 4
11. Switch the valve 4 open to the outside of the system to remove any air in the line
12. Once there is no air in the line, switch valve 4 to connect line 8 and line 5
13. Allow the injection to continue.
14. Once there is no more air at the exit, slowly increase the back pressure regulator to the targeted pressure of the system.
15. Keep injecting until the system reaches the targeted pressure and the pressure drop across the core is stable.
16. Once the overall pressure is reached and the pressure drop across the core is stable, record the pressure
17. Increase the injection rate to get two more pressure drop across the core sample
18. Record the pressure
19. Stop the brine injection
20. Close valve 2 and 3 to retain the pressure system
21. Switch valve 2 and 3 to connect line 3 and line 7 with the outside of the system.
22. Switch valve 1 to connect line 2 and line 3
23. Inject acidic sample fluid using ISCO pump #2
24. Allow the acidic fluid to push any air and brine out through valve 2 and 3.
25. Once the air and brine in the lines are replaced by acidic sample solution, close valve 2 and 3.

26. Since the valve 2 and 3 are closed and the ISCO pump is injecting, the pressure in the line from the transfer cylinder 2 to the valve 2 and 3 will increase. Allow the pressure to increase to match the system pressure.
27. Once the line pressure reaches the previous pressure, stop the ISCO pump #2 and switch valve 2, and 3 to connect lines between the valves.
28. Start injecting the acidic sample solution
29. Record pressure flux across the core sample
30. Stop the injection once it reaches 2 pore volume
31. Quickly switch valve 2 and 3 to the open position (connect with the outside of the system)
32. Switch valve 1 to connect the line 1 and line 3
33. Inject brine to push any acidic solution and air form the lines.
34. Once the acidic solution and air are gone, close the valve and keep injecting the brine until the lines from the pump to valve 2, 3 and 7 reaches the pressure system.
35. Once it reaches the pressure of the system, switch the valve to connect the lines between the valves.
36. Inject the brine and record the pressure drop across the core sample, once the pressure is stable
37. Increase the injection pressure to get 2 more values.

4.8 Fracture conductivity measurement

An acid-fracture conductivity measurement setup is a tool for measuring conductivity that is caused by a simulated acid fracturing process in a laboratory. The setup simulates the fracture in

the formation created after well stimulation, along with the pressure and temperature at the fracture. The International Organization for Standardization (ISO) has written a standard of procedures for measuring the long-term conductivity of proppants [41]. The ISO procedure recommends the fluid and material used in the experiment, apparatus, and the steps for setting up a conductivity cell, acquiring data, as well as calculations. The setup can be used to measure conductivity of proppants under closure stress. However, there is not a procedure determined by the ISO for measuring a conductivity that has been created after an acid etches the surface of the core sample and a closure stresses applied. Regardless, there are setups that were created by other researchers to study the acid fracturing stimulation and measure a conductivity after acid etching [42, 43, 44, 45]. Barron et al.'s acid fracturing setups was one of the earliest setup that was used for studying the effect of velocity of the flowing acid and width of the fracture on reaction rate [42]. Anderson and Fredrickson developed the setup for optimizing the process by studying the effect of kinetic parameter and rock characteristic during acid fracturing [43]. Navarrete et al. used the acid conductivity measurement setup to study the low reaction rate acid and compare its results with the results produced from 28% hydrochloric acid [44]. Zou designed a setup and created a procedure for an experimental apparatus for dynamic fracture conductivity testing [45]. The setup simulates the fracture in the vertical direction and is able to inject a flow rate of 1 L/min (Figure 16).

Figure 16: A conductivity measurement set up by Zou [45]

Fracture width created after the fracturing of the formation is very difficult to measure. Therefore, many researchers have used the term of fracture conductivity for representing the ability of flow in the fracture by keeping the term of permeability and width of the fracture together hence, multiplying the permeability and the width of the fracture. This calculation of fracture conductivity is based on the modified Darcy's law which is shown as equation 2

$$k_f w = -\frac{q\mu L}{h\Delta P} \qquad \text{Equation 2}$$

Where:

h	=	Fracture height (ft)
$k_f w$	=	Fracture conductivity (D·ft)
l	=	Length (ft)
ΔP	=	Pressure difference (atm)
q	=	Flow rate (mL/s)
μ	=	Viscosity (cp)

The acid conductivity experiment tests the ability of the Ultra Series FF-01 product in substituting hydrochloric acid in acid fracturing. An acid fracturing set up initially relied on the flow of 2% KCl through fracture gap (width) to build the required system pressure. This was followed by injection of acid solution. After completing the acid etching time, the gap is closed and 2% KCl is flowed once more for measuring conductivity. The core used for this test is Lueders Limestone. The setup is composed of 3 major parts. There are pumps, a hydraulic press, and a conductivity cell. The pump used for this setup is a Teledyne ISCO Series D Dual-Pump Continuous Flow System. The dual-pump offers a continued injection during the experiment. The maximum injection rate for this pump is 500 mL/min. The conductivity cell is made from Hastalloy which can resist 15% HCl. The cell dimensions are shown in the diagram below (Figure 17 and Figure 18) and conductivity cell with cell piston is shown in Figure 19.

CELL

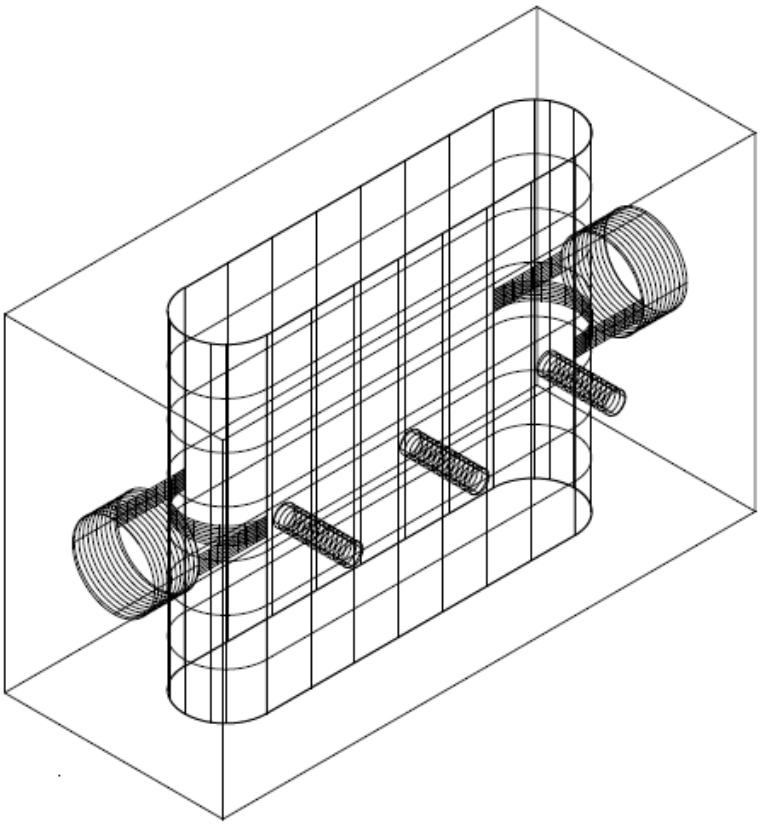

Figure 17: A conductivity cell

CELL MEASUREMENT

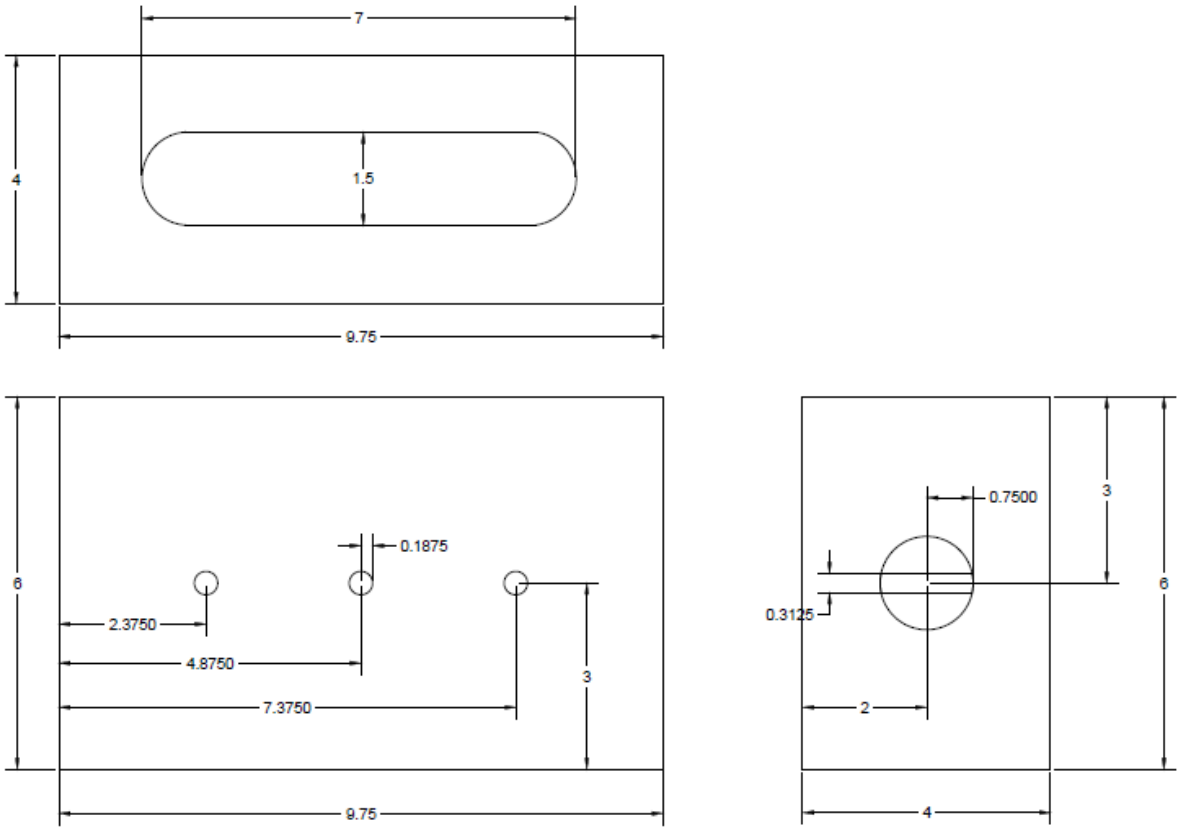

Figure 18: A conductivity cell dimensions

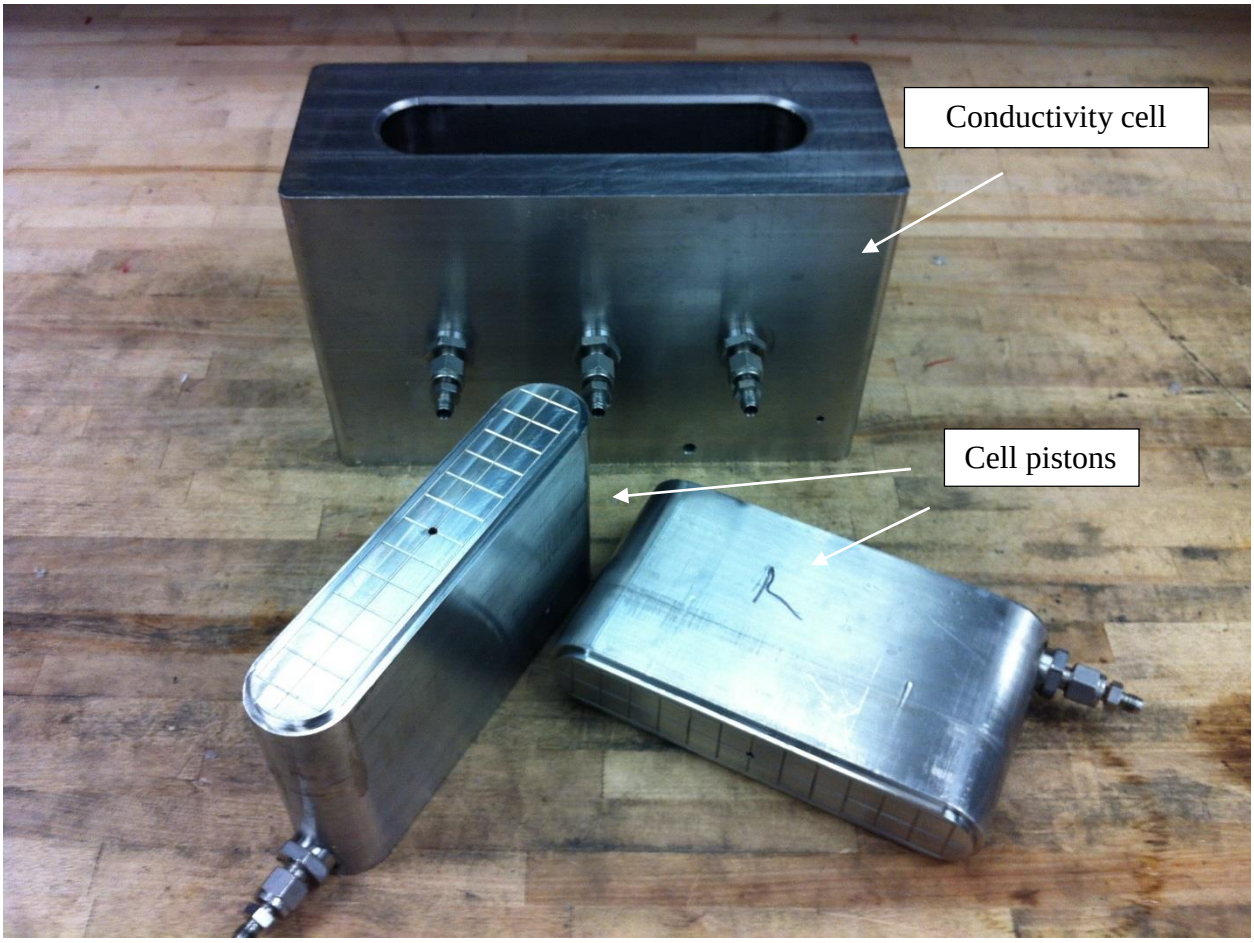

Figure 19: A conductivity cell with its side pistons

The setup was designed to handle pressure up to 2500 psi to ensure that CO_2 generated from the reaction of acidic solution and the carbonate rock is kept in the system and do not cause two phase flow. Figure 20 is shows the schematic of acid fracturing measurement setup. The following are the steps followed during each test:

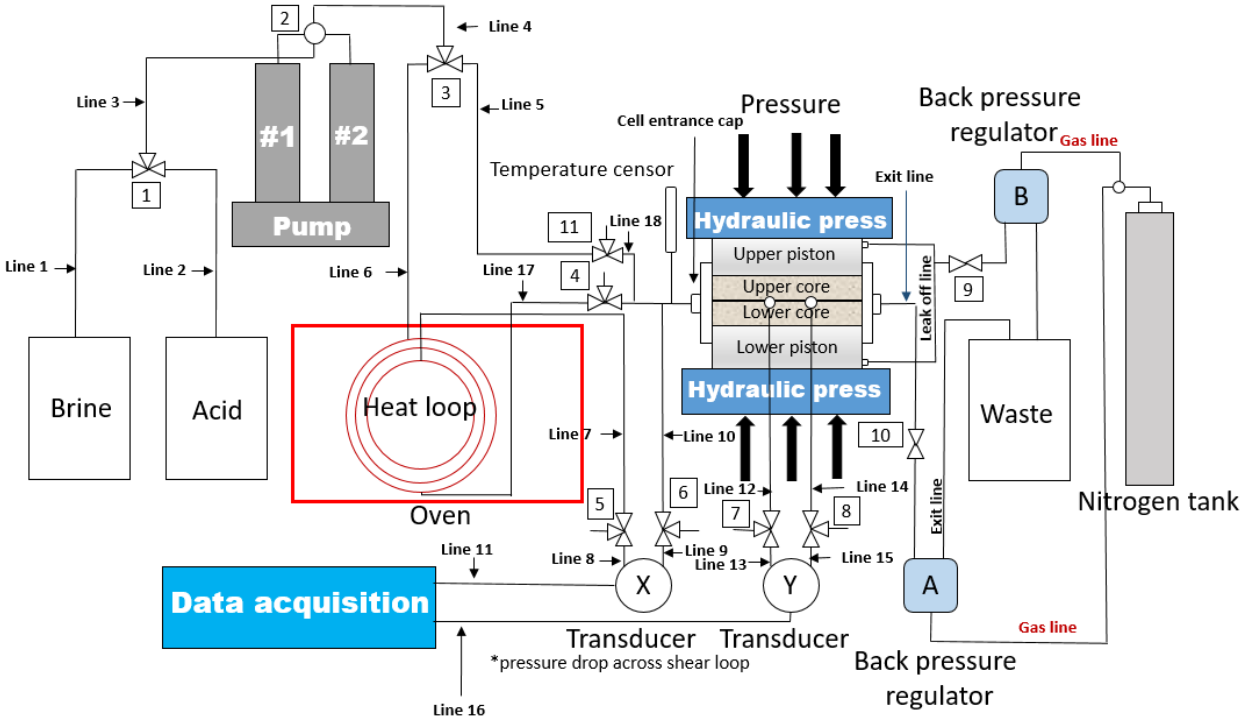

Figure 20: Schematic of the acid fracturing test

1. Seal the side of the core samples with 100% silicon using a mold.
2. Once the seal is dried, core samples are inserted into the cell chamber by applying the pressure from the hydraulic press but leave the spacing between the cores (fracture width) for 0.3125".
3. To prevent leaking, the tiny gap between the conductivity cell and the core samples are sealed with silicon.
4. Let the sealant dry before inserting the pistons into the set up.
5. Fill transducers and transducer lines 8, 9, 11, 13, and 15, with mineral oil.
6. Once the sealant is dried, insert the piston into the cell chamber and set the conductivity cell in the hydraulic press.
7. Switch valve 1 to connect line 1 and line 3.

8. Bypass heat loop by switching valve 3 to connect line 4 and line 5 (this bypassing prevents dilution of acid sample in the heat loop).
9. Switch the valves 4, 6, 7 and 8 open to the outside of the system to remove any air in the lines (bleeder valve).
10. Switch valve 11 to connect line 5 and line 18.
11. Begin the process by injecting 2% potassium chloride (KCl).
12. Inject 2% KCl at the rate of 10 mL/min using a dual-pump for a continuous flow system (Teledyne Isco) to fill a simulated fracture gap (width) and saturate the core samples.
13. Turn on the oven and slowly increase the heater to a targeted temperature.
14. Once there is no more air at valve 4, switch valve 4 to close position.
15. Once there is no more air at valve 6, close valve 6 to prevent damaging the transducer.
16. Allow the injection of 2% KCl until there is no more at valve 7, switch valve 7 to a close position.
17. Once there is no more air at valve 8, switch valve 8 to a close position.
18. Let the injection to continue until there is no more air in the exit line.
19. To ensure the core sample is fully saturated, reduce the injection rate to 2 mL/min, close the exit valve (10) and open the leak off valve (9). Thus force the 2% KCl to flow through the core samples.
20. Allow the injection of 2% KCl to continue until no air in the leak off lines.
21. Turn on the heater (hydraulic press plates and heat wrapped) to raise the temperature of the set up to desired temperature.
22. Once there is no more air in the leak off line, open the exit valve (10) to remove any air trapped in the exit line.

23. Continue to inject to build pressure by slowly increasing the back pressure regulator at the exit lines (A) and the leak-off line (B).
24. After the system reached the desire pressure, stop the pump.
25. Switch valve 11 open to the outside (retain the pressure in the system)
26. Empty the 2% KCl in the pump through valve 11.
27. Once the pump is empty, close valve 11.
28. Switch valve 3 to connect line 4 with line 6.
29. Switch valve 4 and 5 open to the outside of the system (removing any air in the heat loop).
30. Switch valve 1 to connect line 2 and line 3.
31. Start filling and injecting acid using the dual-pump at the rate of 20 mL/min.
32. The acid solution is injected through the loop which is inside the oven. This is done to allow acid solution to increase its temperature to targeted temperature before entering the conductivity cell.
33. Once there is no air at valve 5, close valve 5.
34. Allow injection until there is no air in the heat loop.
35. Once there is no more air at valve 4, close valve 4.
36. Continue to inject to build pressure.
37. Once the pressure in the lines and heat loop are equal the pressure of the system, stop the dual-pump and switch valve 4 to connect line 17 and 18.
38. At the same time, switch valve 5 to connect line 7 and 8 and valve 6 to connect line 9 and 10.
39. Start to inject the acid sample solution for one hour at the rate of 100 mL/min.

40. After completing the etching time, stop the pump.
41. Switch valve 4 to a close position.
42. Slowly switch valve 3 to connect line 4 and line 5.
43. Turn off all the heaters.
44. Release pressure in line 2, 3, 4, and 5 by slowly switch valve 11 open to the outside.
45. Quickly remove any remaining acid sample solution in the cylinder 1 and 2 by pumping out through valve 11.
46. Once the cylinder 1 and 2 are empty, switch valve 1 to connect line 1 and line 2.
47. Start the pump to inject 2% KCl.
48. Once there is no more air at valve 11, close valve 11.
49. Allow the pump to continue injection.
50. Once the pressure in line 5 equal to that of the system, stop the pump.
51. Switch valve 11 to connect line 5 and line 18.
52. Inject 2% KCl at the rate of 20 mL/min for removing any acid and residue left in the fracture.
53. Allow the injection for 90 minutes (cleanup period).
54. Once the cleanup period is completed, stop the injection.
55. Slowly reduce the pressure of the system by carefully and slowly reduce the pressure of the back pressure regulator A and B to room condition.
56. Open the cell entrance cap.
57. Then, carefully close the simulate gap by applying the pressure from the hydraulic press (closed gap is at the center of the cell chamber).
58. Switch valve 4, 6, 7, and 8 open to the outside.

59. Start injecting 2% KCl at the rate of 5 mL/min.
60. Once there is no more air at valve 4, close valve 4.
61. Once there is no more air at valve 6, close valve 6.
62. Once there is no more air at valve 7, close valve 7.
63. Once there is no more air at valve 8, close valve 8.
64. Once there is no more air at the exit line. Close valve 10.
65. Allow the injection to continue until there is no more air at the leak off line.
66. Once there is no more air at the leak off line, close valve 9.
67. Open valve 10.
68. Allow the injection to remove any remaining air in the system.
69. At the same time switch valve 7 to connect line 12 and line 13 and valve 8 to connect line 14 and line 15.
70. Increase the back pressure regulator A to 500 PSI.
71. At the same time switch valve 7 and valve 8 to a close position.
72. Reduce the injection rate to 0.2 mL/min.
73. Increase a closure stress to 1000 PSI by applying a pressure using the hydraulic press.
74. At the same time switch valve 7 to connect line 12 and 13 and valve 8 to connect line 14 and 15.
75. Allow the injection of 2% KCl to continue.
76. Once a pressure different is stable, record the pressure different.
77. Apply a pressure using the hydraulic press for conductivity measurement at different closure stress.
78. The test is repeated with different acid fracturing fluids.

79. Again, repeat the procedure with different leak off pressures.

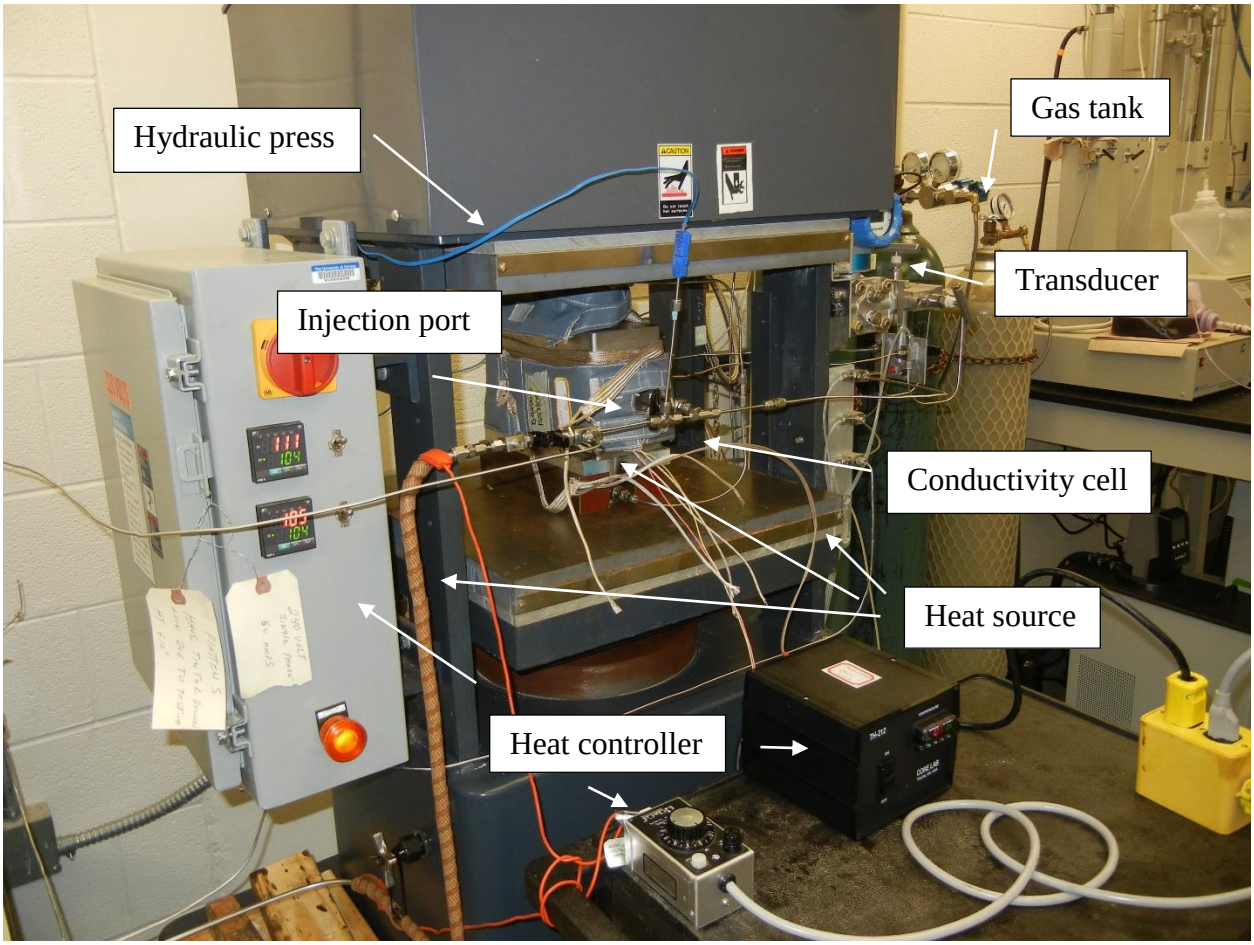

Figure 21: The conductivity measurement setup

Figure 20 is the conductivity measurement setup during the experiment. A closer look of the conductivity cell on the hydraulic press during the experiment can be seen in Figure 21.

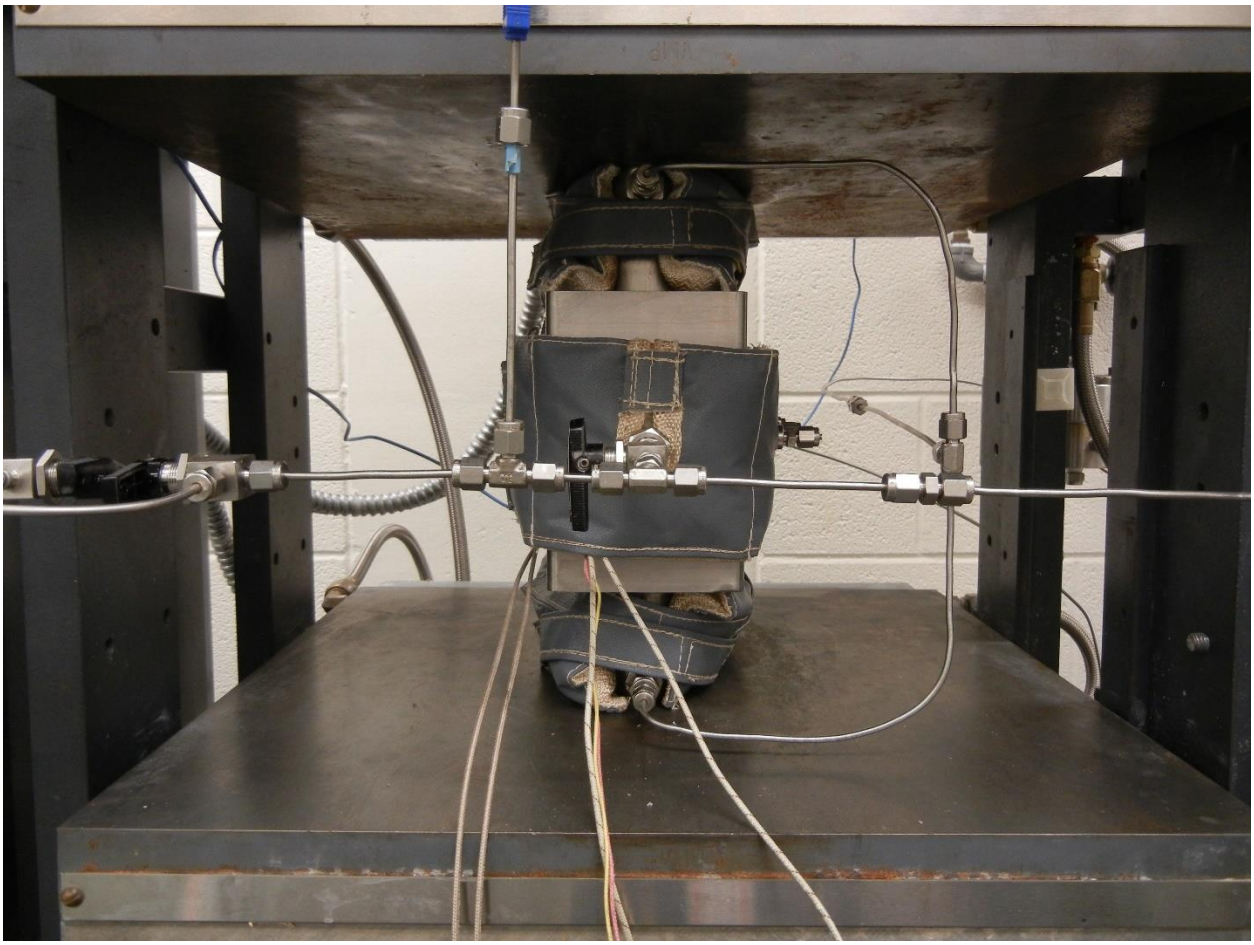

Figure 22: The conductivity cell during the experiment.

As one would expect, the injected acidic solution for acid fracturing process will react with calcium carbonate as soon as they come in contact with each other. As a result, the reaction takes place from the early point of the fracture and continues to react along the fracture path before it reaches the fracture tip. Thus, the amount of spent acid in the injected acidic solution will increase as the acidic solution moves to the end of the fracture. One of the factors that dictates the increase in the amount of the spent acid before it reaches the end of the fracture, is the rate of acid reaction. Different acidic solutions will react at different rates. thus the amount of the spent acid in the fracture will not be the same while using different acidic solutions for acid fracturing treatment.

Therefore, the acid conductivity test was modified by adding a reactor with a calcium carbonate powder to the experimental setup. Addition of the reactor in the setup allows us to simulate the reaction inside the fracture where acidic solution reacts with the calcium carbonate first before it reaches the core samples. A fracture size in Appendix A, property of a calcium carbonate powder, and the ratio of the reaction rate of the Ultra Series FF-01 and $CaCO_3$ to 15% HCl and $CaCO_3$ from the beaker testing for the reaction rate was used for determination of how much calcium carbonate powder is needed in each experiment. The schematic of the conductivity measurement with a reactor added is shown in Figure 23.

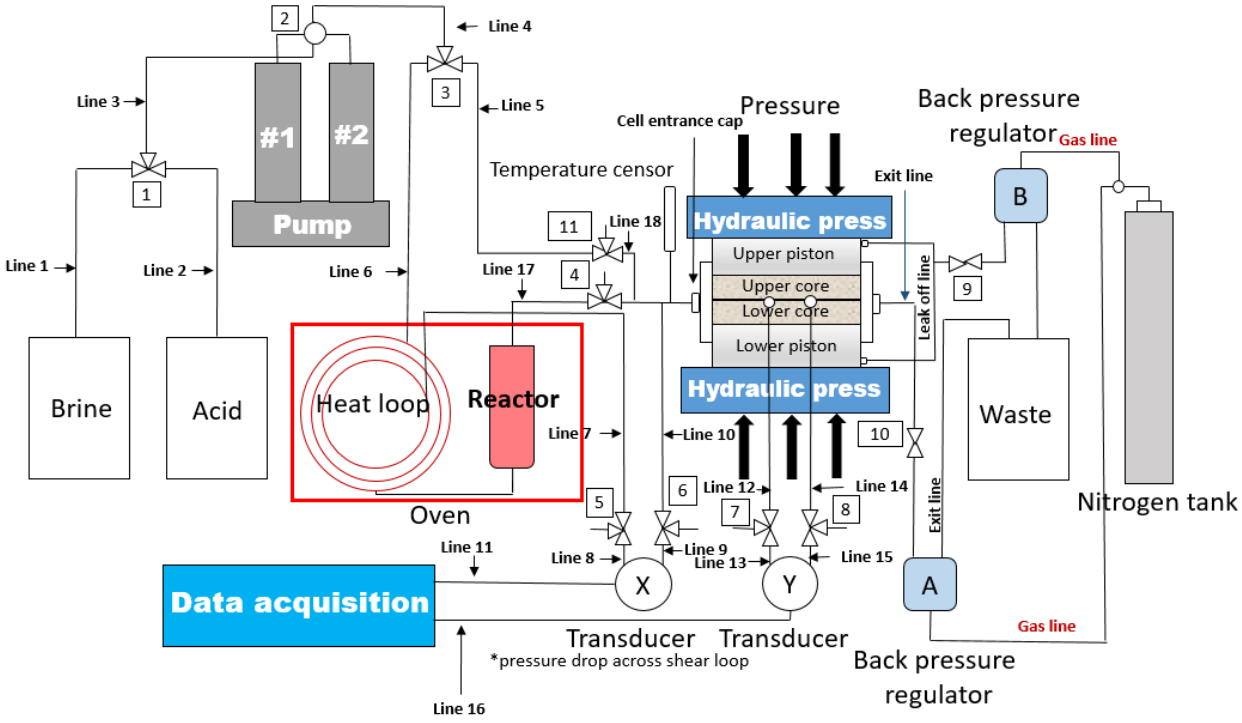

Figure 23: Schematic of the acid fracturing test with a reactor added.

5. Results and discussion

In this section the negative impacts of 15% HCl and its additives to environment and human health will be discussed. Results of studies, conducted to test the ability of Ultra Series FF-01 to substitute the commercial 15% HCl with additives, have also been explained. The experiments have been divided into seven parts, namely, beaker testing for corrosion, beaker testing for reaction rate, beaker testing for emulsion, IFT measurement, viscosity test at the interface of the sample acid and sample crude oils, core flooding tests to study the ability to generate wormholes and increase permeability after matrix acidizing, and acid-fracture conductivity measurements to study the ability of Ultra Series FF-01 to etch the surface of the carbonate core samples compared to HCl.

5.1 Impact of using 15% HCl and its additives in well treatment on human health and environment

The effect of conventional acidizing fluid on environment and human health is a matter of concern. The MSDS shows HCl can cause burning and irritation to skin and eyes. If ingested, it can cause damage to internal tissues, circulatory failure, and corrode human esophagus and stomach. In addition, breathing in HCl can cause damage to respiratory system. Moreover, a long term exposure to HCl can develop chronic bronchitis symptoms can which lead to breathing difficulties, inflammation of skin, and photosensitization [28, 30]. Furthermore, many of the additive chemicals used in well treatment are ‘F-grade’ hazardous chemicals according to QCAT. There is a lack of information regarding toxicity for many other chemicals while the names of some others have not even been released to the public [3, 2]. Moreover, hydrochloric acid was evaluated using QCAT guidelines. It receives a grade C from QCAT. The result indicates that hydrochloric acid is a moderate concern chemical substance but a safer chemical is preferred. On the other hand, the

QCAT gives a grade A to the Ultra Series FF-01 for preferable chemical. It is degradable and has minimum effect on human health and marine's life.

5.2 Beaker testing to measure corrosion rate

The beaker tests designed to study the effect of the sample acid on the stainless steel plate showed a mass reduction when the stainless steel plate was left in 2% KCl in 15% hydrochloric acid and a slightly reduction when it was left in 15% HCl with additives for 24 hours. The loss in weight implies that stainless steel plate was dissolved and that during the acidizing process, the products of this reaction will affect the solution. The increase of iron ion in the reservoir, coupled with the pH level raised caused by spent acid after well stimulation, promotes iron precipitation. Consequently, it reduces the ability of crude oil to flow. On the other hand, the mass of stainless steel plate that was left in the beaker containing 2% KCl in the Ultra Series FF-01, did not change. Table 2 shows a 10.12% and 0.289% mass reduction of stainless steel when it was left inside 2% KCl in 15% HCl and 15% HCl with additives, respectively for 24 hours.

Table 2: Stainless steel dissolving in sample acidic solution.

Time (hrs.)	Stainless steel in 15% HCl with additives weight (g)	Stainless steel in 2% KCl in 15% HCl weight (g)	Stainless steel in 2% KCl in FF-01 weight (g)
0	27.71	27.77	27.69
1	27.70	27.74	27.69
2	27.70	27.69	27.69
4	27.70	27.61	27.69
6	27.69	27.58	27.69
9	27.68	27.01	27.69

12	27.66	26.68	27.69
16	27.65	25.89	27.69
20	27.64	25.10	27.69
24	27.63	24.96	27.69

The effect of 15% HCl on stainless steel can clearly be seen in Figure 24 (left and center) while the stainless steel plate in the Ultra Series FF-01 is still shinny after 24 hours in the solution (right).

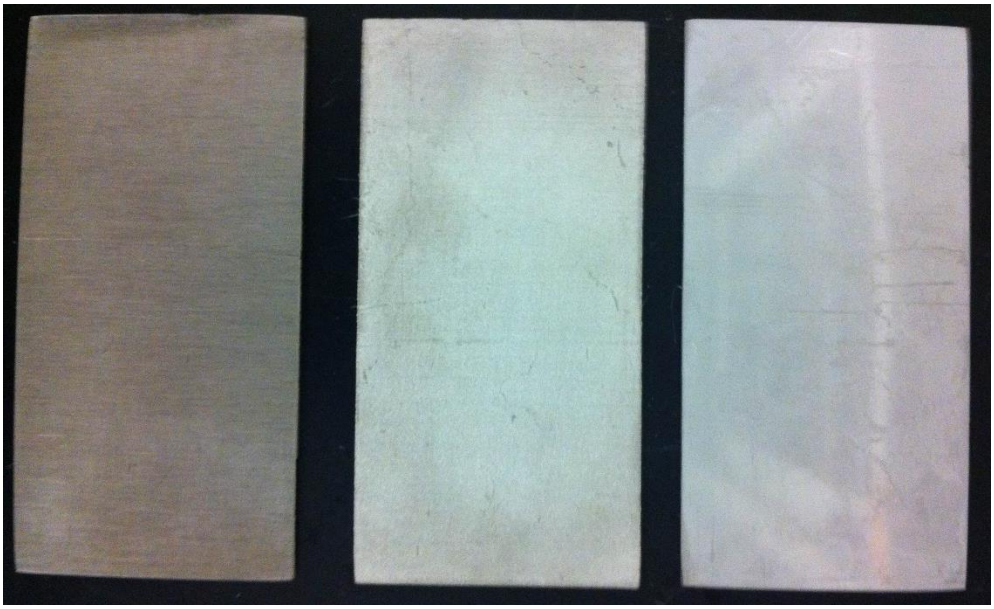

Figure 24: (Left) Stainless steel plate in 15% HCl with additives, (Center) Stainless steel plate in 2% KCl in 15% HCl, and (Right) Stainless steel rod in 2% KCl in the Ultra Series FF-01 after 24 hours.

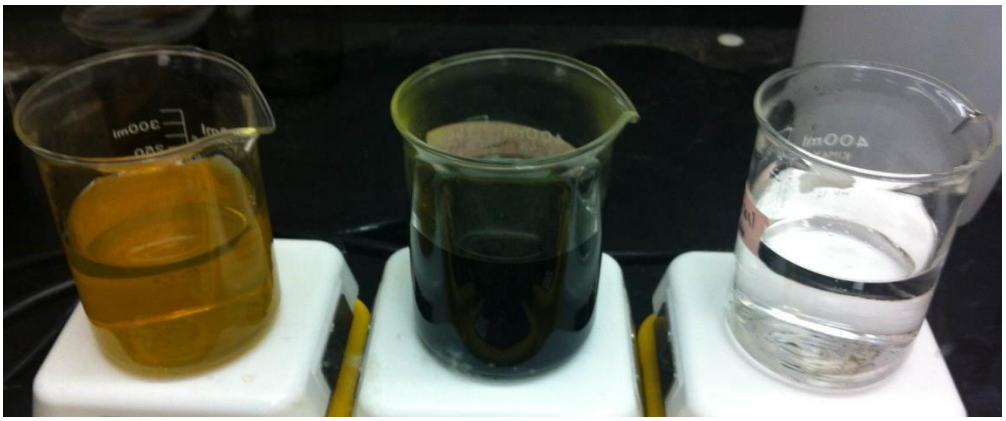

Figure 25: (Left) 15% HCl with additives, (Center) 2% KCl in 15% HCl, and (Right) 2% KCl in the Ultra Series FF-01 after 24 hours with stainless steel plate.

Figure 25 shows the color of acidic solution samples after the experiment. The 2% KCl in 15% HCl color (center) was changed from no color (clear) to a dark green. In comparison, the color of 15% HCl with additives (left) and the Ultra Series FF-01 (right) did not change.

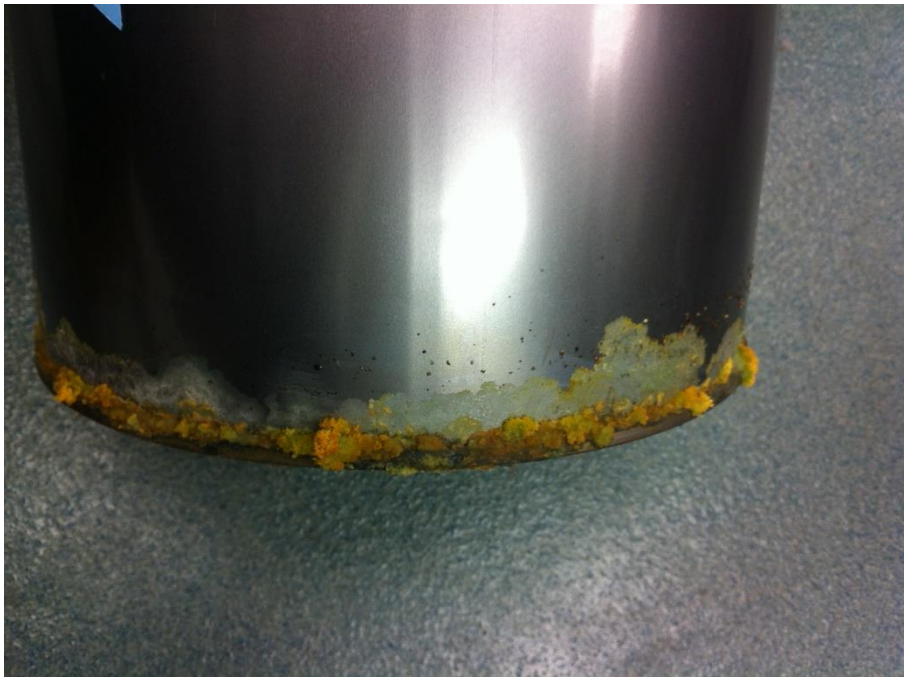

Figure 26: A stainless steel container was corroded by 15% HCl.

During the experiment, an empty HCl container was left in the laboratory. After a week, the container showed rust around its bottom part as can be seen in the Figure 26.

5.3 Beaker testing for rate of reaction

The results of the beaker testing for rate of reaction by adding the $CaCO_3$ powder into the acid samples show 15% HCl has a faster rate of reaction than the Ultra Series FF-01. In the first five minutes 15% HCl dissolved $CaCO_3$ powder five times faster than the Ultra Series FF-01 and three times faster once they reached 20 minutes. This slow reaction rate of the Ultra Series FF-01 can benefit the ability of the acid to penetrate deeper into the formation by reducing the spending rate at the first contact. Thus, it may increase the permeability of the formation after well acidizing.

Table 3: Time vs amount of $CaCO_3$ dissolved in the acid samples.

Time (min)	$CaCO_3$ powder dissolved in FF-01 (g)	$CaCO_3$ powder dissolved in 15% HCl (g)
5	7.23	34.97
10	12.52	47.94
15	16.77	56.63
20	19.33	61.00

5.4 Emulsion testing

Often, well acidizing has run into problems causes by emulsion from mixing acidizing fluid with crude oil. The beaker testing was used to test and compare the emulsion formation after acid samples contacted Lansing Kansas City (LKC) crude oil at the temperature of 40° C. It is cleary seen in a Figure 27 that 15% HCl and LKC crude oil created the emulsion from the first contacted and became stable through twenty fourth hour.

Figure 27: 15% HCl with LKC crude oil in the container at 40° C after shaking (top left), 2 hours (top right), 12 hours (bottom left), and 24 hours (bottom right).

The formation of emulsion can reduce the ability of crude oil to flow, impact injectivity, and increase treatment cost. Thus, additives were introduced in the commercial fluid for well acidizing to prevent the formation of emulsion. Figure 28 shows the 15% HCl with non-emulsifier, along with iron control, corrosion inhibitor, and micro emulsion surfactant formed a lesser emulsion with LKC crude oil than the 15% HCl without any additives and LKC crude oil. However, there is a layer of the emulsion between the 15% HCl with additives and LKC crude oil. Furthermore, there are noticeable crude oil droplets on the glass container.

Figure 28: 15% HCl with additives and LKC crude oil in the container at 40° C after shaking (top left), 2 hours (top right), 12 hours (bottom left), and 24 hours (bottom right).

Finally, Figure 29 shows the Ultra Series FF-01 which is the environmentally friendly product and LKC crude oil produced a little layer of emulsion after second hours. However, the emulsion reduced after twelfth hours and was invisible after twenty fourth hour. The separation of the Ultra series FF-01 and LKC crude oils was cleared and there was no evidence of droplet formed after the mixing of the Ultra Series FF-01 and LKC crude oil.

Figure 29: The Ultra Series FF-01 with LKC crude oil in the container at 40° C after shaking (top left), 2 hours (top right), 12 hours (bottom left), and 24 hours (bottom right).

It is clearly from the experiment that the Ultra Series FF-01 without any additives does not produce stable emulsion or any crude oil droplet with LKC crude oil. In addition to the beaker testing for emulsion, the Ultra Series FF-01 was tested to find an interfacial tension values with LKC crude oil at the atmospheric pressure and the temperature of 40° C.

Table 4: The interfacial tension values at each FF-01 concentration in 2% KCl at atmospheric pressure and the temperature of 40° C.

% Concentration of FF-01 in the 2% KCl	IFT values (dynes/cm)
100	4.95
50	12.49
10	15.60
0	20.49

Table 4 shows that the lowest interfacial tension value was at 100% of the Ultra Series FF-01. The IFT value increases as the concentration of the Ultra Series FF-01 decreases. Moreover, the additional experiment for IFT measurement was done at the pressure of 500 psig and the temperature of 40° C. The results in Figure 30 shows the IFT values of the Ultra Series FF-01 and LKC crude oil at atmospheric pressure and 500 psig are in the same trend and were not affected by the increased pressure.

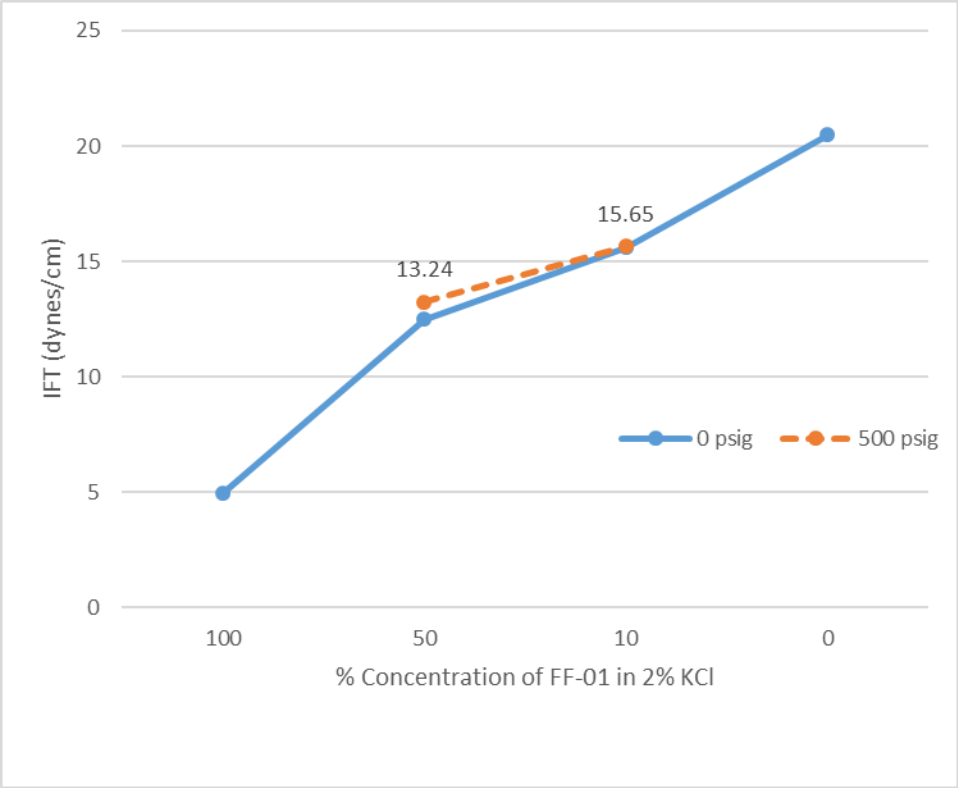

Figure 30: A plot of IFT values versus % concentration of FF-01 in 2% KCl at atmospheric pressure compares to 500 psig at 40° C.

Lastly, the LKC crude oil droplet in the 50% of the Ultra Series FF-01 and 50% of 2% KCl at the temperature of 40° C, and at the atmospheric pressure and 500 psig can be seen in Figure 31 and Figure 32 respectively.

Figure 31: The image of the LKC droplet in 50% FF-01: 50% of 2% KCl at the atmospheric pressure and the temperature of 40° C.

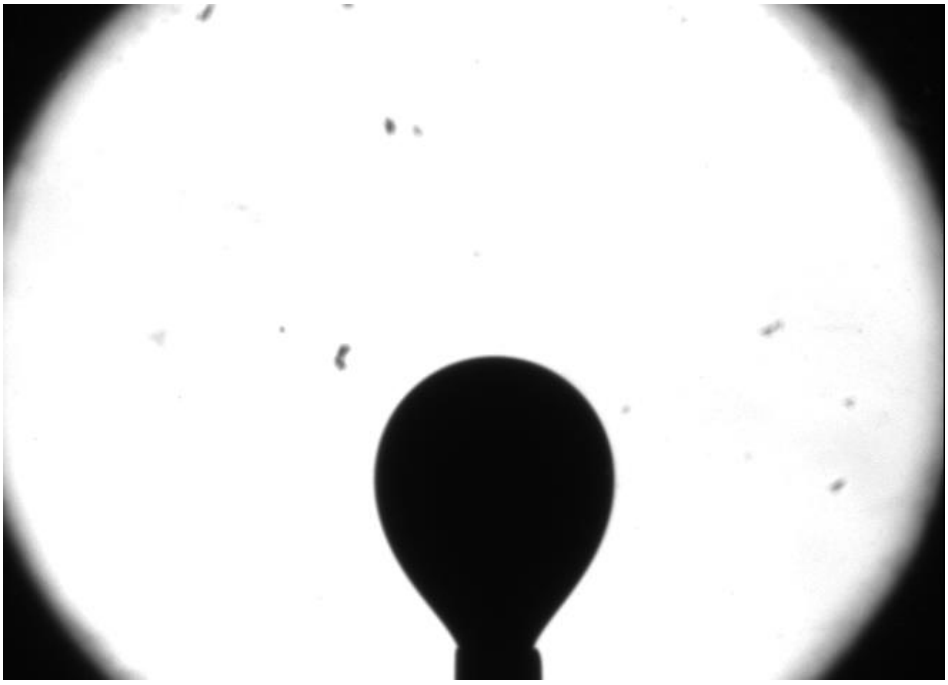

Figure 32: The image of the LKC droplet in 50% FF-01: 50% of 2% KCl at the pressure of 500 psig and the temperature of 40° C.

5.5 Viscosity testing using Brookfield viscometer

The crude oil sample, at the interface between Lansing Kansas City (LKC) crude oil and the acid solution (Table 5), was collected. Viscosity was measured at a temperature of 40° C at different shear rate values, using a Brookfield viscometer. The fluid sample that was at the interface of Lasing Kansas City crude oil and the Ultra Series FF-01 had the lowest viscosity at all shear rates. This is favorable for the acidizing process.

Table 5: Crude oils and acid solution used during viscosity test

Lansing Kansas City crude oil + 15% HCl
Lansing Kansas City crude oil + 15% HCl with additive*
Lansing Kansas City crude oil + The Ultra Series FF-01
Mississippian crude oil + 15% HCl
Mississippian crude oil + 15% HCl with additive*
Mississippian crude oil + The Ultra Series FF-01

*These additives are 3 ppm of iron control additive, 2 ppm of non-emulsifier additive, 2 ppm of corrosion inhibitor additive and 1 ppm for micro-emulsion surfactant.

The results suggest that the sludge formed during acidizing process using Ultra Series FF-01 is less viscous than the sludge formed using 15% hydrochloric acid alone, and 15% hydrochloric acid along with the additives. The same results were obtained for the Mississippian limestone crude oil. It is also worth noting that there is not any residue or emulsification after the Ultra Series FF-01 contacted Lansing Kansas City and Mississippian crude oil. A plot of shear rate versus viscosity

of Lansing Kansas City with acid samples and Mississippi crude oil with acid samples can be seen in Figure 33 and Figure 34 respectively.

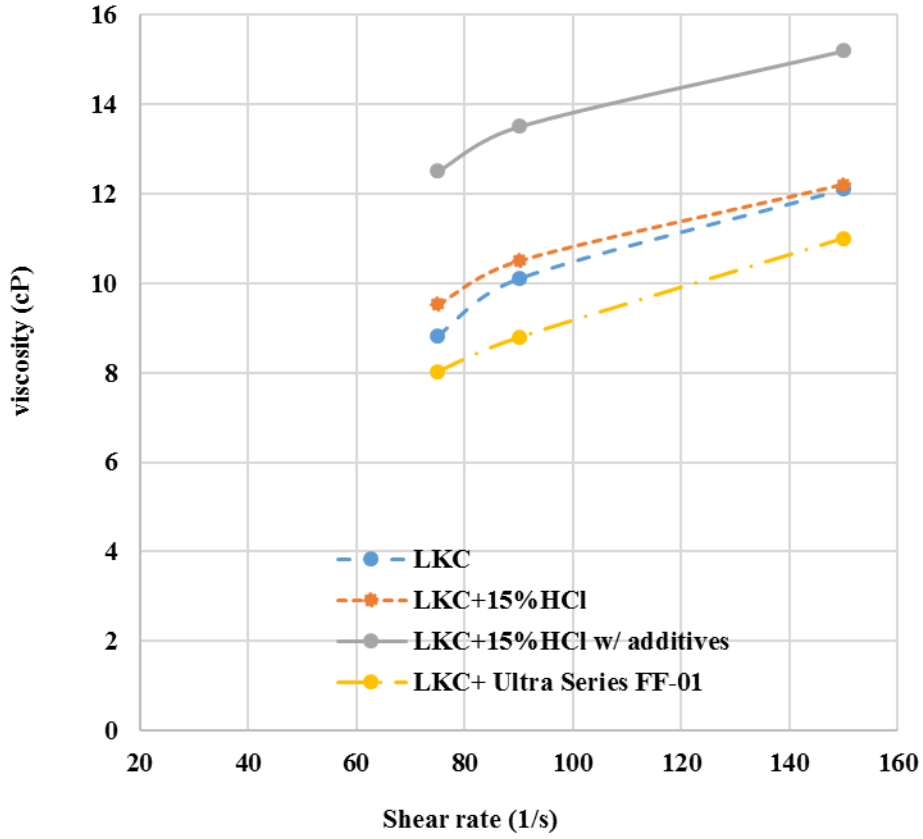

Figure 33: Viscosity at the interface of Lansing Kansas City crude oil and acidic solutions at different shear rates

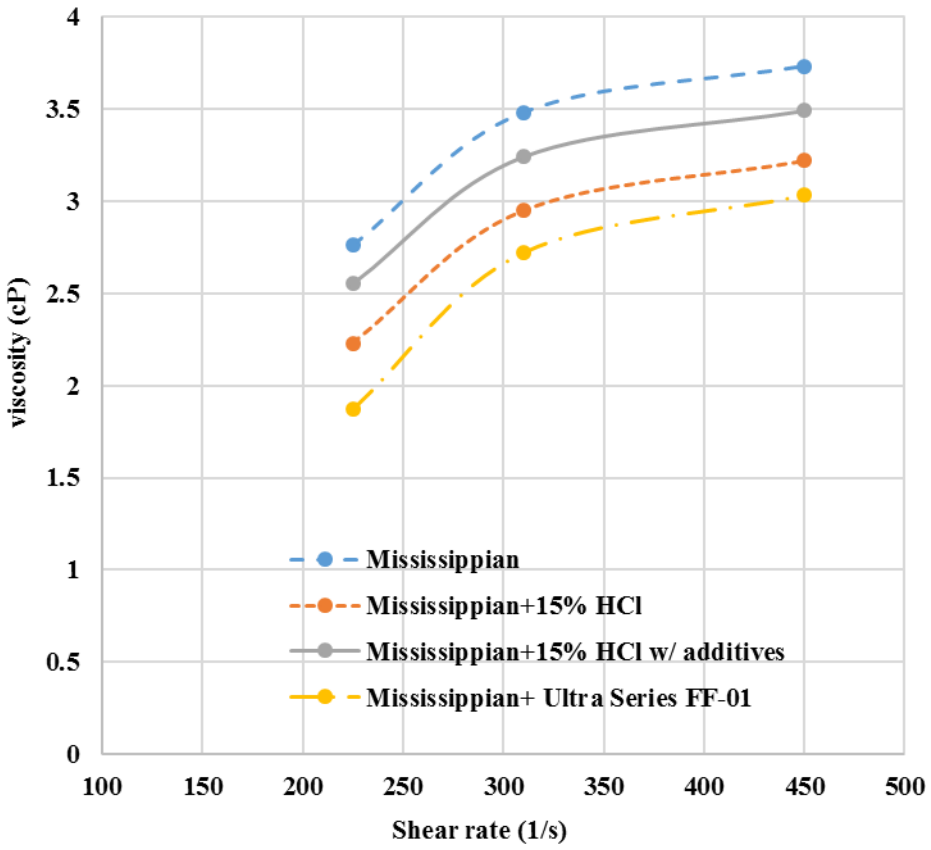

Figure 34: Viscosity at the interface of the Mississippian crude oil and the acidic solutions at varying shear rates

The field's shear rates were calculated by following the study of Zitha et al [46]. The results from the calculation were in the rage of 1-1000 1/s. Thus, the viscosity results from the experiments are within the field's condition.

5.6 Core flooding test results

Many core flood experiments were performed to study the performance of the Ultra Series FF-01 at various operating conditions to compare it with that of 15% HCl. The parameters that were changed are the type of acid solution, temperature, overall pressure, and initial permeability of the core sample (low, medium, and high permeability cores). The amount of acid solution sample used for all these experiments was 2 pore volume of the core plugs. Various studies were conducted by

keeping one parameter constant at a time and changing others, and the result have been included in the next section.

5.6.1 Injection rate effect

Injection rate is one of the important factors during well acidizing. Each formation requires an appropriate injection rate to maximize wormholes while it is also important to prevent downhole pressure from damaging the formation and equipment during the operation. Thus, it is important to study the effect of injection rate for each acid solution sample. Table 6 summarizes the entire experiment at the injection rate of 0.5, 1, 2, and 4 mL/min where the fixed parameters are the temperature (40°C) and the back pressure (1000 psi). Results of the experiment show that Ultra Series FF-01 performed better than 15% HCl when a lower injection rate (0.5 mL/min) was used. This finding totally agrees with the previous study by Markey et al [39].

Table 6: Experiment results where the injection rate is changing but the temperature and back pressure are fixed

Acid Type	q, (mL/min)	T, (C)	Back pressure, (psi)	Average k factor increase	Standard deviation
FF-01	0.50	40	1000	20.34	0.25
15% HCl	0.50	40	1000	2.36	0.00
FF-01	1	40	1000	23.57	4.56
15% HCl	1	40	1000	31.39	0.00

FF-01	2	40	1000	35.17	9.87
15% HCl	2	40	1000	70.89	21.34
FF-01	4	40	1000	23.99	8.32
15% HCl	4	40	1000	42.21	12.86

The reaction rate of HCl is much higher than that of FF-01 which results in causes spent faster by reacting just at the surface if the injection rate is low. Higher injection rate helps HCl to go deeper into the core sample and generate wormholes. FF-01 on the other hand has a lower reaction rate and so it doesn't get spent easily at the surface allowing it to go deeper into the core surface and generate wormholes. Therefore, at the injection rate of 0.5 mL/min, FF-01 gives better results as compared to HCl based on the experiments. Figure 35 compares the permeability factor increase caused by 15% HCl with that of Ultra Series FF-01.

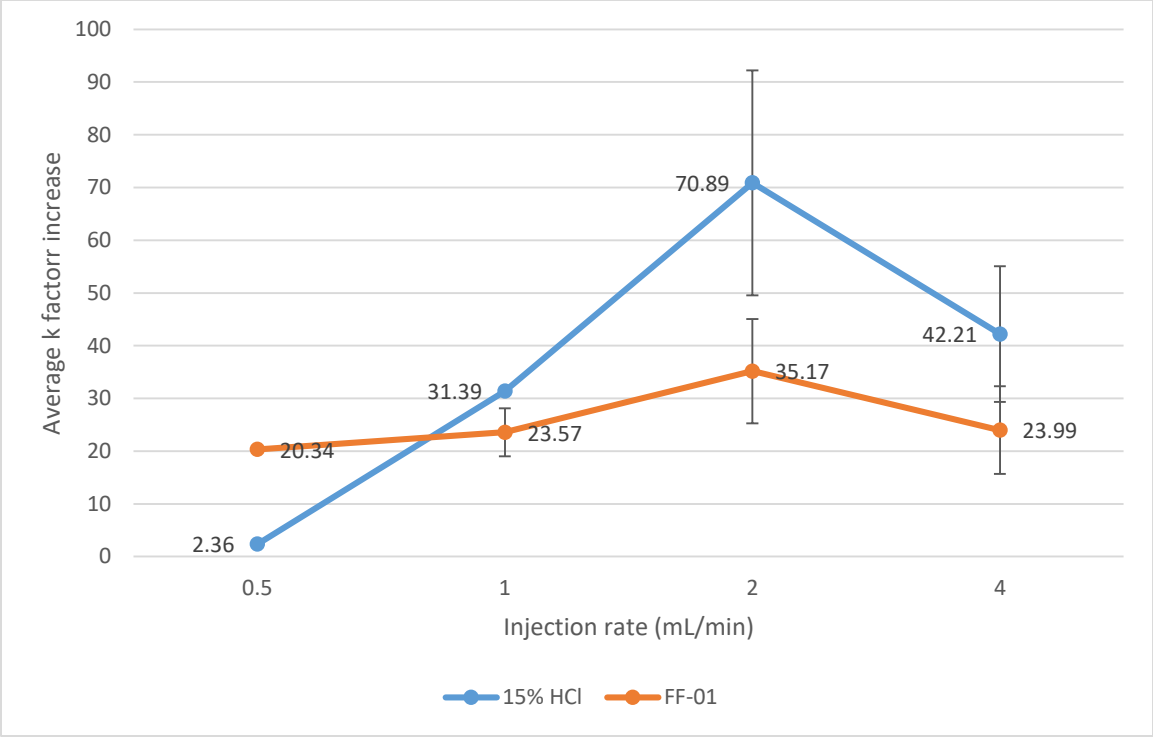

Figure 35: A graph of permeability factor increase vs injection rate at 40 C and 1000 psi comparing the performance of 15% HCl with FF-01

5.6.2 Effect of temperature on matrix acidizing

Temperature is one of the parameter that vary during well acidizing. It is important to get a basic understanding of how the Ultra Series FF-01 would perform when compared with 15% HCl under different temperatures. Three temperature conditions were studied to see the effect of the final permeability after matrix acidizing. The three temperatures were 25, 40 and 70 °C while the fixed parameters were the back pressure at 1000 psi and the injection rate at 2 mL/min. Table 7 shows that the results of core-flooding by Ultra Series FF-01 and HCl showed a similar trend when the temperatures were varied. The increase in permeability factor was higher for 15% HCl than for Ultra Series FF-01 in all three temperatures. They performed better at the temperature of 40° C as compared to 25° C and 70° C. However, the permeability factor increased caused by 15% HCl to hit a maximum at 40 degrees after which it started dropping shapely while the permeability factor

increased caused by the Ultra Series FF-01 decreases slightly when the temperature increased from 40 °C to 70 °C. This might imply that 15% HCl require a higher flow rate when the temperature increases due to increase in rate of reaction. The Ultra series FF-01 shows a better potential to increase permeability at higher temperatures if this trend of permeability factor increase versus temperature in Figure 36 holds true. The results are summarized and shown in Table 7.

Table 7: Experiment results when temperature is changing but the injection rate and back pressure are fixed

Acid Type	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k, (mD)	Final k, (mD)	k factor increase
FF-01	IL-A41	2	25	1000	192.20	5197.00	27.04
15% HCl	IL-A57	2	25	1000	169.68	8508.90	50.15
FF-01	IL-A10	2	40	1000	167.60	3678.30	44.84
15% HCl	IL-A14	2	40	1000	190.25	14087.24	74.05
FF-01	IL-A55	2	70	1000	126.40	4498.40	35.58
15% HCl	IL-A51	2	70	1000	216.78	11147.80	51.43

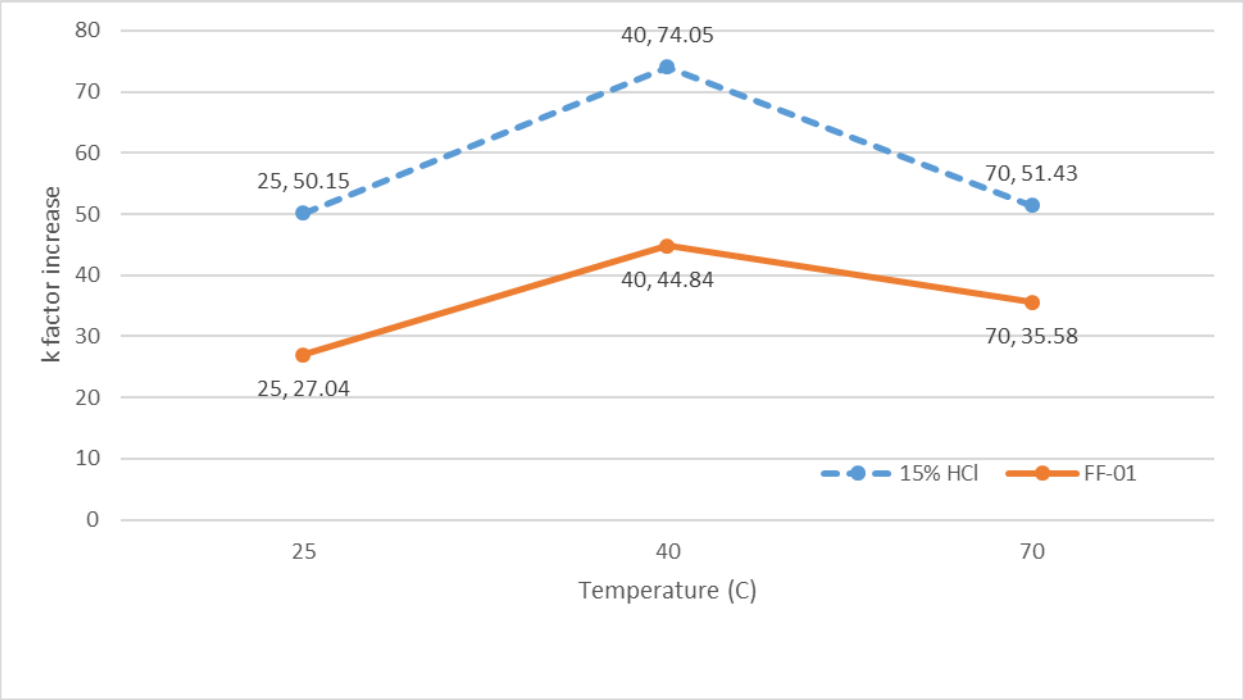

Figure 36: A graph of permeability factor increase vs temperature

5.6.3 Effect of back pressure during matrix acidizing

CO_2 is formed during reaction of acidizing fluid and carbonate rock. It can impact the ability of acid samples to generate wormholes during matrix acidizing. Thus, various values of back pressure were used and studied during experiments. The back pressure used during this experiment were 14, 500, and 1000 psi while the injection rate was kept constant at 2 mL/min and the temperature was 40°C. Table 8 shows that the ability of acids to increase permeability are highest when the back pressure was at 1000 psi for 15% HCl and the Ultra Series FF-01. This explains the importance of applying back pressure during matrix acidizing. Furthermore, the result shows permeability variation for HCl solution was much higher than that in the case of FF-01. 15% HCl acid was unable to generate a breakthrough wormhole when the back pressure was at atmospheric pressure, while the Ultra Series FF-01 increased the permeability factor by 26.54 times. At back

pressure values of 500 psi and 1000 psi, the results of FF-01 and 15 % HCl were almost comparable. At 1000 psi back pressure, the CO_2 produced from the reaction stayed inside the fluid completely and hence didn't affect the results. At lower back pressure values, the produced CO_2 in its gaseous form is thought to have impacted the process negatively thus reducing the ability of acids to increase the permeability. Looking at the results, one would assume that the effect of CO_2 is more prominent in the case of HCl than for FF-01. More studies have to be done into the chemical properties of FF-01 to shed more light into this phenomenon. The results are summarized in the Table 8 and plotted in Figure 37.

Table 8: Experiment results where the back pressure is changing but the injection rate and temperature are fixed.

Acid Type	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k, (mD)	Final k, (mD)	k factor increase
FF-01	IL-A48	2	40	14	214.04	5660.50	26.54
15% HCl	IL-A54	2	40	14	230.42	230.42	1.00
FF-01	IL-A47	2	40	500	208.80	5983.90	28.66
15% HCl	IL-A67	2	40	500	271.63	9042.10	33.29
FF-01	IL-A46	2	40	1000	213.00	6437.60	30.22
15% HCl	IL-A64	2	40	1000	255.08	12175.8	47.73

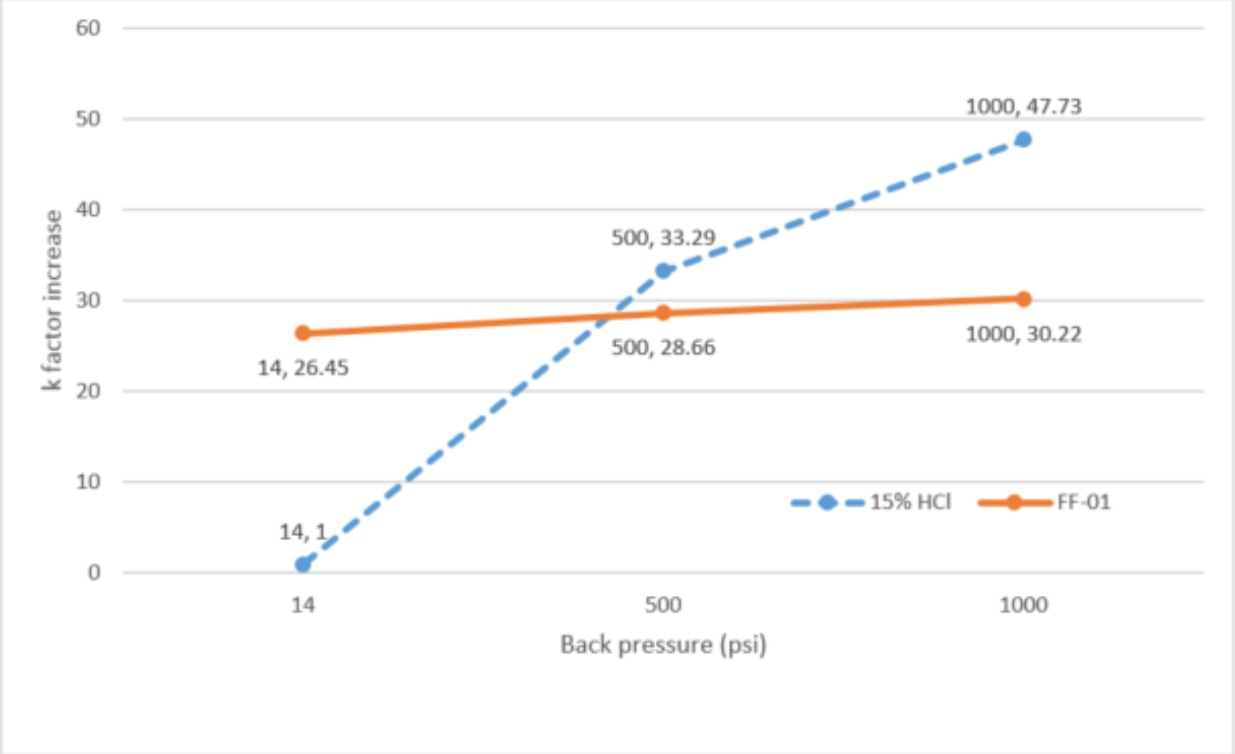

Figure 37: A graph of permeability factor increase vs back pressure

5.6.4 Effect of initial permeability

The core plugs were grouped into three based on their initial permeability: high (greater than 250 mD), medium (50 – 250 mD), and low (less than 5 mD). The purpose of this division was to study whether the initial permeability of the core sample has an effect on the ability of the 15% HCl and the Ultra Series FF-01 to generate wormholes during matrix acidizing. All experiments used a rate of injection at 2mL/min, the back pressure was 1000 psi and the temperature was at 40°C. The result show that 15% HCl was able to create higher permeability factor increase in all groups when compared to the Ultra Series FF-01. It is worth mentioning that 15% HCl and the Ultra Series FF-

011 generated highest permeability factors increase with the core plug that had the lowest permeability. The results are summarized and shown in Table 9.

Table 9: Experiment results where the initial permeability is grouped into low, medium, and high but the injection rate, temperature and back pressure are fixed.

Acid Type	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k, (mD)	Final k, (mD)	k factor increase
FF-01*	IL6-2	2	40	1000	0.54	3230.90	5953.00
15% HCl*	IL6-1	2	40	1000	0.56	9548.90	17077.30
FF-01	IL-A44	2	40	1000	167.60	3678.30	44.84
15% HCl	IL-A62	2	40	1000	178.85	12626.10	70.60
FF-01	IL-A10	2	40	1000	275.50	6548.90	23.77
15% HCl	IL-A20	2	40	1000	286.08	12429.40	43.45

* The experimental results are from Markey et al [39].

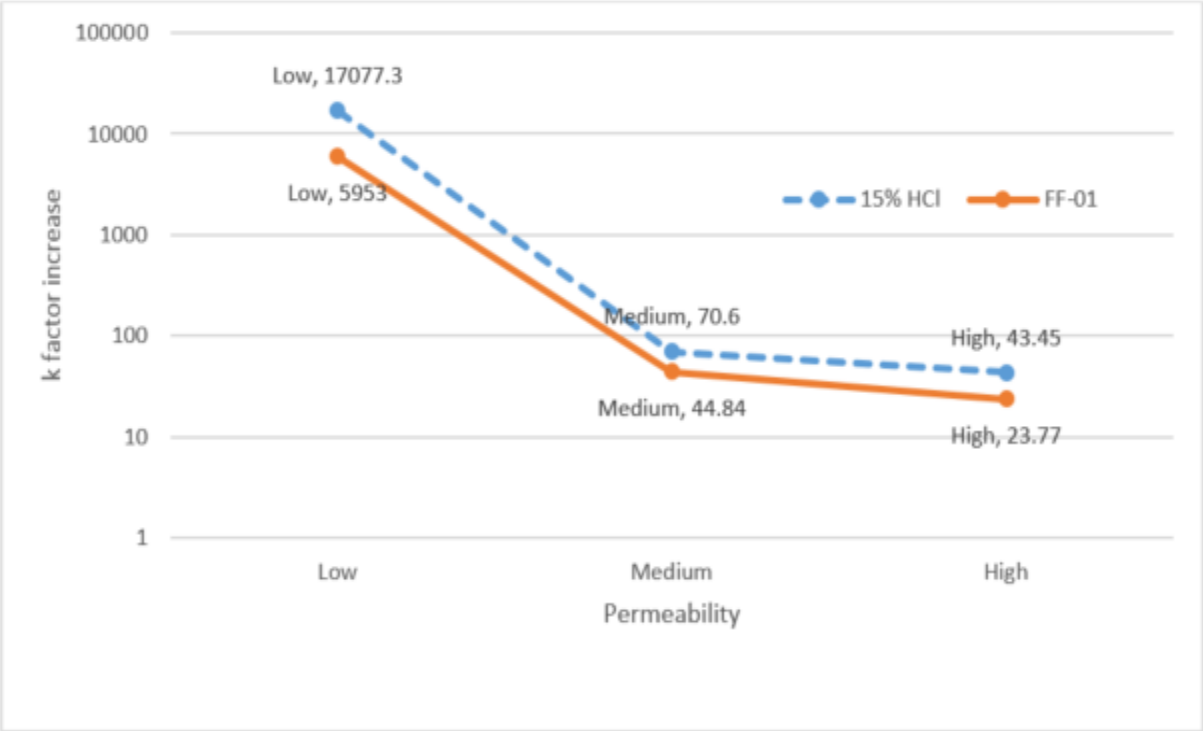

Figure 38: A graph of permeability factor increase vs initial permeability

The results showed a very similar trend between both the acids and the permeability increase was a direct function of the initial permeability as it can be seen in Figure 38.

5.6.5 Mixture of FF-01: 15% HCl

It would be a good idea to use a blend of both 15% HCl acid and FF-01 in acid fracturing operations as both have their own distinct advantages. Moreover, usage of large volumes of environmentally harmful HCl acid can be reduced by promoting the use of environmentally friendly Ultra Series FF-01. Mixing FF-01 to 15 % HCl might slow down the reaction rate of HCl solution while maintaining the ability to create wormholes thus maximizing permeability by penetrating deeper into the core. It was decided to keep all operating parameters like temperature, injection rate and back pressure constant and then vary the ratio of FF-01 to HCL mixture. Tests were conducted

using different mixture ratios: 1:1,2:1, and 3:1 and finally pure FF-01 while keeping temperature constant at 40□C, injection rate at 2mL/min and back pressure at 1000 psi. The results interestingly show that the ratio 2: 1 of Ultra Series FF-01 to 15% HCl produced the maximum permeability factor increase which is better than the ratio of 1:1. The results are summarized in the Table 10 and plotted in Figure 39.

Table 10: Experiment results where the acid ratio of FF-01 to 15% HCl is changing but the injection rate, temperature and back pressure are fixed.

Acid Type (FF-01 to 15% HCl)	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k, (mD)	Final k, (mD)	k factor increase
1 to 1	IL-A52	2	40	1000	180.95	9903.90	54.73
2 to 1	IL-A81	2	40	1000	152.52	9400.20	61.63
3 to 1	IL-A56	2	40	1000	146.81	7783.70	53.02
FF-01	IL-A44	2	40	1000	158.08	6611.80	41.83

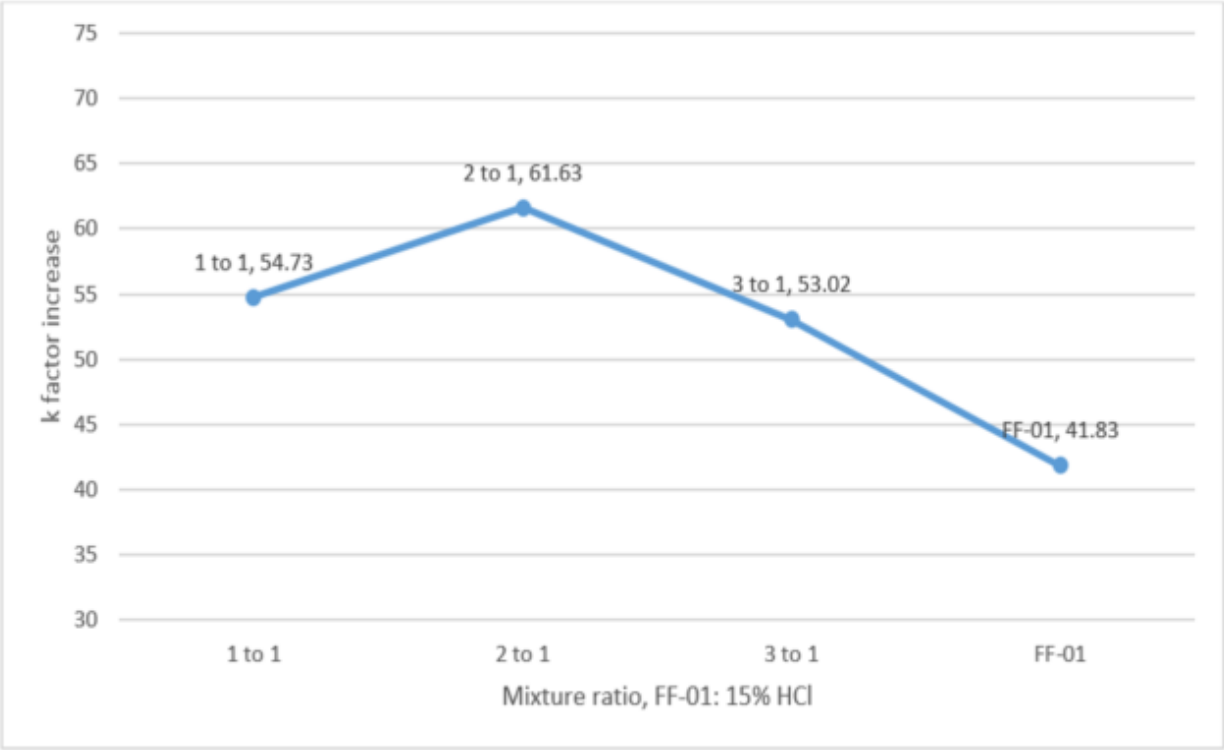

Figure 39: A graph of permeability factor increase vs mixture ratio of FF-01 and 15% HCl

5.6.6 Dilution

The effect of concentration of FF-01 solution on permeability enhancement was tested. FF-01 was diluted to 90%, 75% and 50% concentrations. It was decided to keep all operating parameters like temperature, injection rate, and back pressure constant as in the case of the previous tests. Finally, pure FF-01 solution was also used as a baseline test. The dilution of the Ultra Series FF-01 decreased its ability to generate wormholes. Figure 40 shows a decreasing tend in permeability when the extent of dilution increases. The results are summarized and shown in the Table 11.

Table 11: Experiment results where the concentration of the Ultra Series FF-01 is changing but the injection rate, temperature and back pressure are fixed.

Acid Type (% concentration of FF-01)	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k, (mD)	Final k, (mD)	k factor increase
50%	IL-A40	2	40	1000	313.00	2526.90	8.07
75%	IL-A45	2	40	1000	269.10	2414.70	8.97
90%	IL-A49	2	40	1000	336.40	4646.10	13.81
100%	IL-A38	2	40	1000	275.50	6548.90	23.77

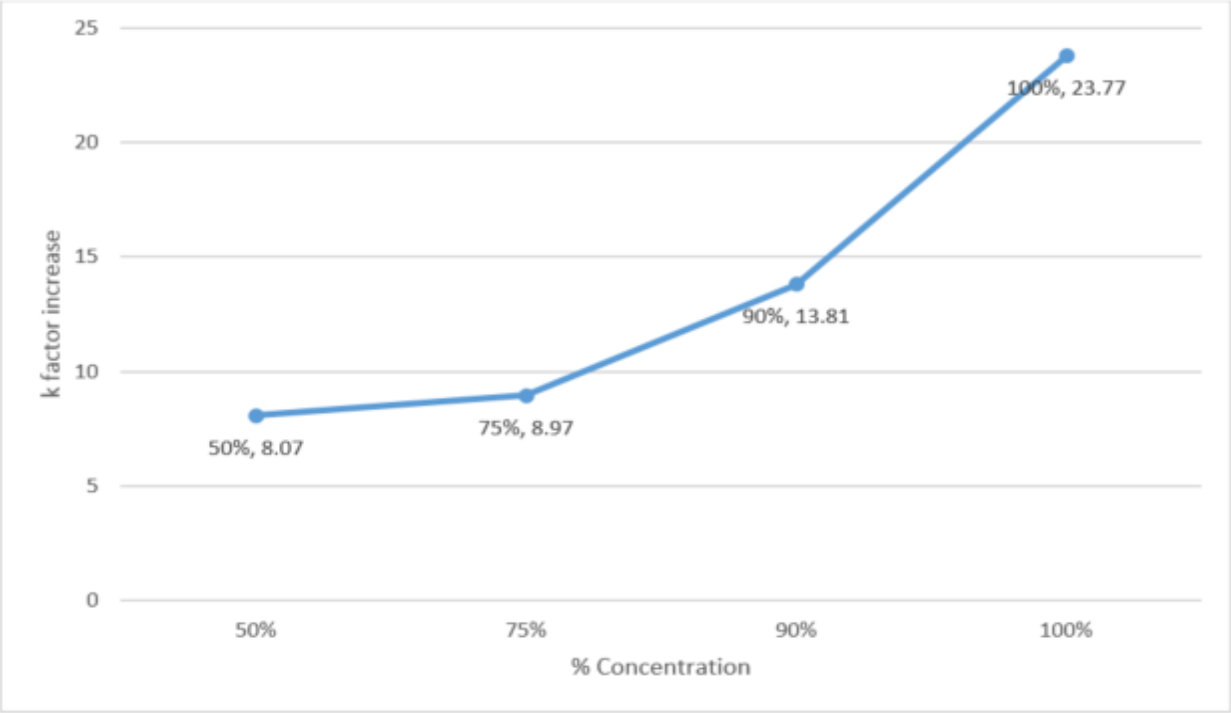

Figure 40: A graph of permeability factor increase vs % concentration of the Ultra Series FF-01

5.6.7 Acid type

It was decided to try combinations of different type of acids and compare their performances with respect to each other. It was decided to keep all operating parameters like temperature, injection rate, back pressure constant like in the previous case and then vary the acid types. The results show that 15% HCl with additives provides the best results in term of increasing permeability, as it doubles the permeability factor increase when compared to the Ultra Series FF-01. However, 15% HCl with additives come with many negative impact to human health and environment. The results are summarized and shown in the Table 12 and graphed in Figure 41.

Table 12: Experiment results where type of the acid is changing but the injection rate, temperature and back pressure are fixed.

Acid Type	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k (mD)	Final k (mD)	k factor increase
15% HCl w/ field's additive	IL-A69	2	40	1000	112.84	10909.00	96.68
1 : 1, 10%Acetic Acid : 15%HCl	IL-A66	2	40	1000	167.45	12201.80	72.87
15% HCl	IL-A62	2	40	1000	178.85	12626.10	70.60
2 :1, FF-01 : 15% HCl	IL-A81	2	40	1000	152.52	9400.20	61.63
FF-01	IL-A44	2	40	1000	185.08	6611.80	41.83
10% Acetic acid	IL-A65	2	40	1000	124.72	4854.80	0.70

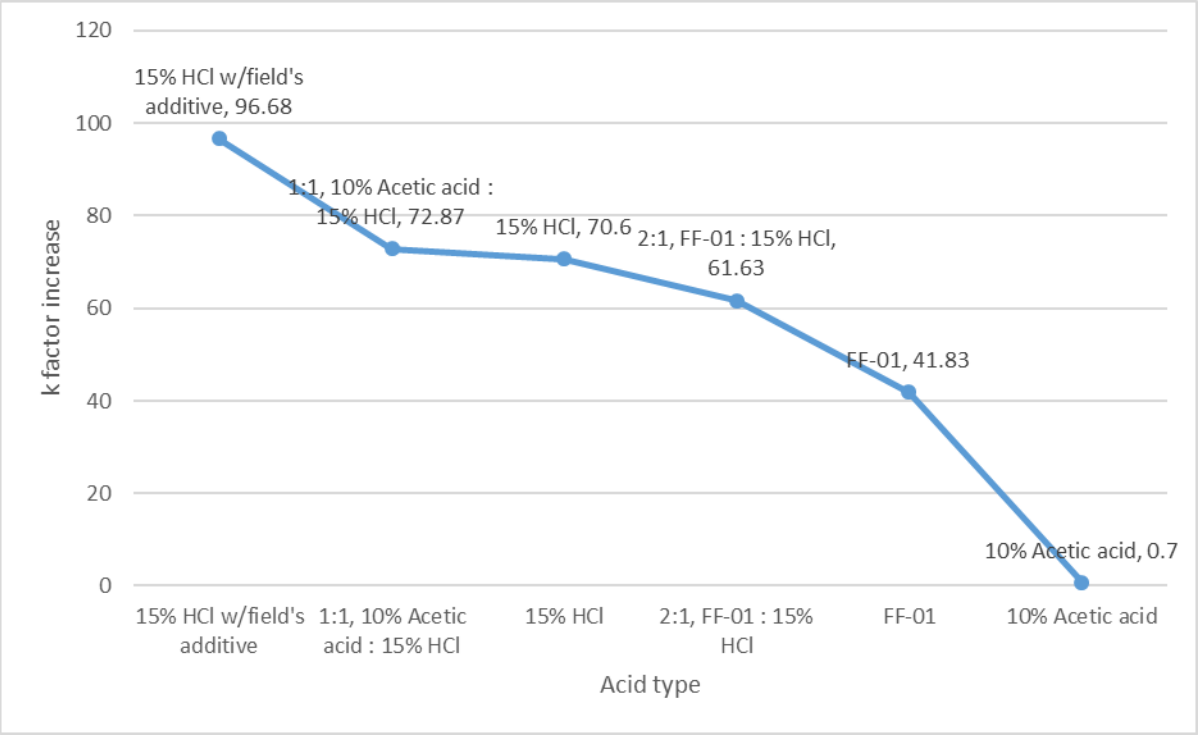

Figure 41: A graph of permeability factor increase vs acid type

It is worth trying 15% HCl with additives with a low flow rate of 0.5 ml/min since 15% HCl without its additives performed poorly at this flow rate. The 15% HCl with additives was used in the experiment where the injection rate was 0.5 mL/min, the temperature was 40 C, the back pressure was 1000 psi and the amount of acidic solution injected was 2 pore volume. Table 13 concludes the results of matrix acidizing using low injection rate (0.5 mL/min) in low permeability cores. When the negative impact on human health and environment are ignored, it is evident (Figure 42) that 15% HCl with its additives are able to generate wormholes and perform better than Ultra Series FF-01. The 15% HCl used without additives was completely used up during the reaction with the surface of the core samples and as a result wormholes were not generated.

Table 13: Experiment results where the acid type is changing but the injection rate, temperature and back pressure are fixed.

Acid Type	Core ID	q, (mL/min)	T, (C)	Back Pressure (psi)	Initial k (mD)	Final k (mD)	k factor increase
15% HCl w/ field's additive	IL-A75	0.5	40	1000	4.59	9712.70	2114.69
FF-01	IL-A73	0.5	40	1000	3.63	1178.50	324.36
15% HCl	IL-A74	0.5	40	1000	4.63	5.50	1.19

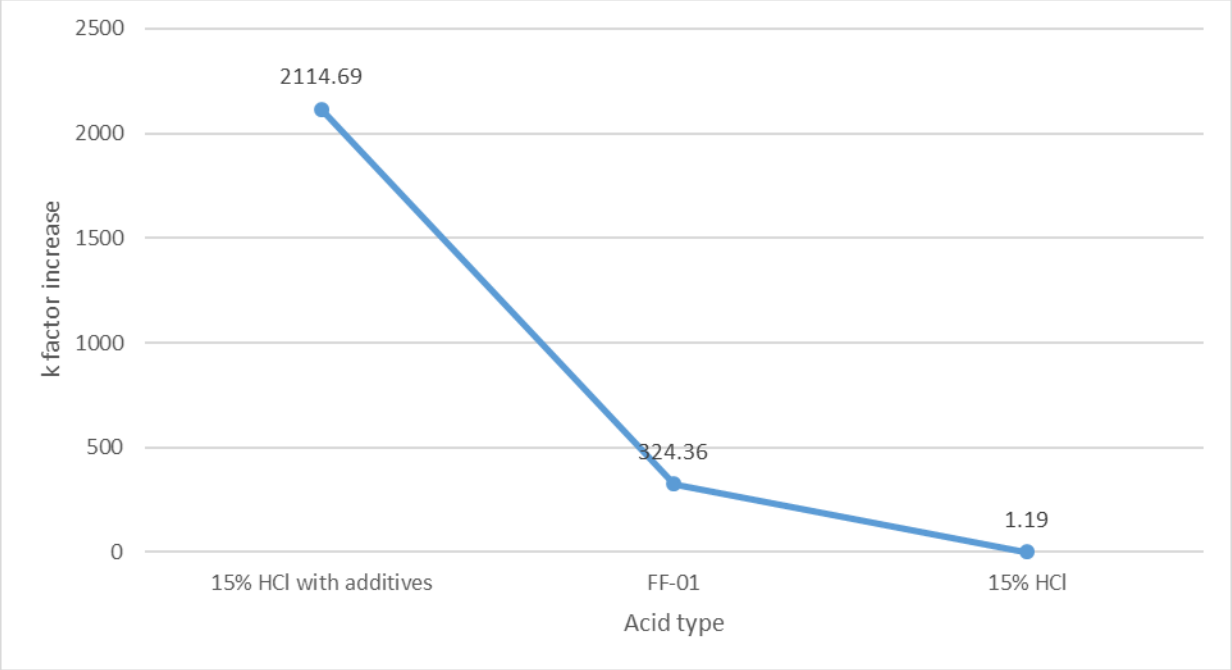

Figure 42: A graph of permeability factor increase vs acid type

The core samples after the test with 15% HCl and additives are shown in Figure 43. The figure shows one big wormhole and many smaller holes at the entrance but it has only one big wormhole

at the exit without any other small holes. Figure 44 shows that when 15% HCl is used without additives, dissolution occurs at the entrance because of the fast reaction of 15% HCl but no wormholes was generated. Figure 45 shows the ability of the Ultra Series FF-01 to generate many wormholes at the entrance as well as the exit. This is an interesting result because the 15% HCl with additive has been shown to create one big wormhole while being unable to divert and generate more than one connected wormhole. However, the Ultra Series FF-01 can generate many connected wormholes. To conclude the results, FF-01 has been found to be generating more wormholes while being safe to human health and environment, but it has also room for improvement to enable it to create bigger connected holes thus doing a better job at increasing permeability.

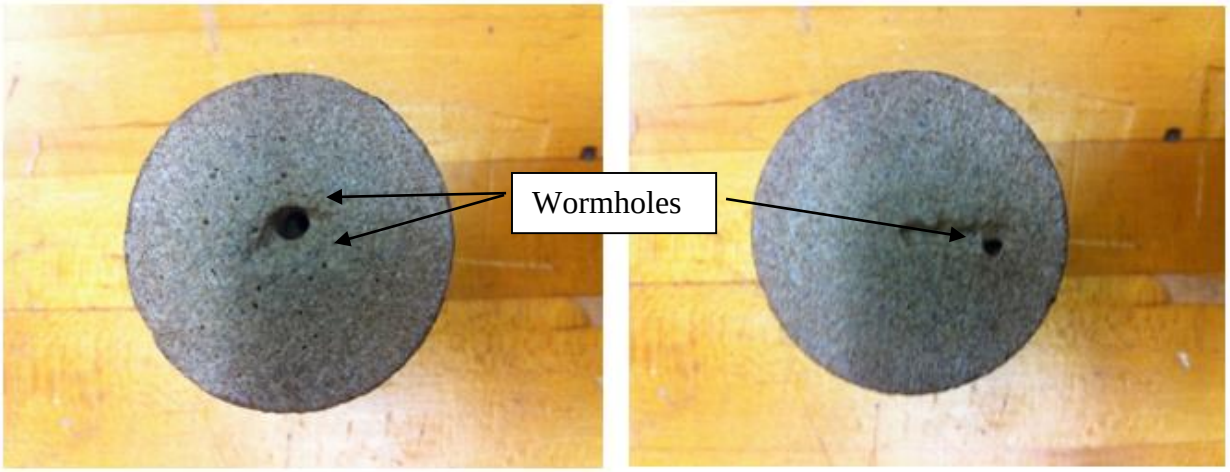

Figure 43: The entrance (R) and the exit (L) of the core sample number IL-A75 after matrix acidizing with 15% HCl and its additives at injection rate of 0.5 mL/min

Figure 44: The entrance (R) and the exit (L) of the core sample number IL-A74 after matrix acidizing with 15% HCl (no additives) at injection rates of 0.5 mL/min.

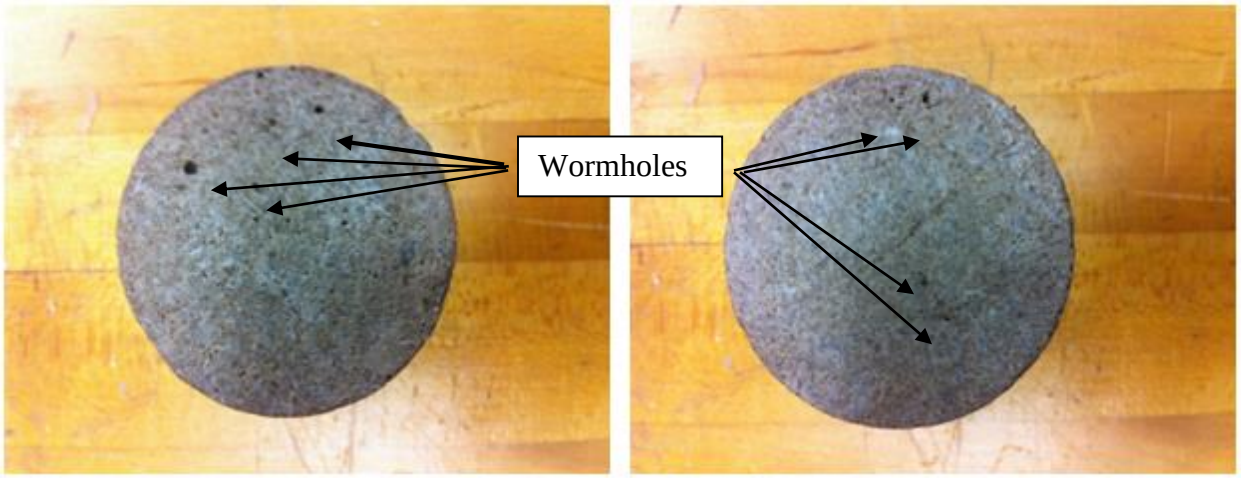

Figure 45: The entrance (L) and the exit (R) of the core sample number IL-A73 after matrix acidizing with the Ultra Series FF-01at the injection rate of 0.5 min/mL

5.7 Conductivity measurements

In this section, conductivity results have been summarized and reported. They have been divided into two parts. The first part is the conductivity results without reactor and the second part is the results of conductivity measurements when the reactor was added into the system.

5.7.1 Conductivity results of the acid-fracture conductivity measurement tests without reactor

The acid-fracture conductivity measurement tests were used to simulate the acid fracturing process. The tests were conducted at the temperature of 40° C. The injection rate was 100 mL/min, the leak off pressure was 100 psi below the fluid pressure, and the total time of injection was 1 hr. The results of the experiment for the Ultra series FF-01 and 15% hydrochloric acid with additives are shown in Table 14 and Table 15 respectively.

Table 14: Experiment results where the FF-01 was used as a fracturing fluid and the leak off pressure was 100 psi lower than system pressure. An injection rate of 4 mL/min was used for a conductivity measurement.

Flow Rate (mL/min)	Stress (PSIG)	BPR (PSIG)	Top Cell - Ceiling (in)	Lower Cell - Floor (in)	Total Clearance (in)	Delta P (PSIG)	kWf (md* ft)
4	1000	508	2.44	2.51	11.05	0.12	741.26
4	2000	508	2.46	2.50	11.01	0.15	571.98
4	3000	508	2.46	2.49	10.95	0.17	504.12
4	4000	508	2.45	2.49	10.90	0.22	386.02

Table 15: Experiment results where the 15% HCl with additives was used as a fracturing fluid and the leak off pressure was 100 psi lower than system pressure. An injection rate of 10 mL/min was used for a conductivity measurement.

Flow Rate mL/min	Stress (PSIG)	BPR (PSIG)	Top Cell - Ceiling (in)	Lower Cell - Floor (in)	Total Clearance (in)	Delta P (PSIG)	kWf (md* ft)
10	1000	715	2.51	2.44	11.04	2.12	118.71
10	2000	715	2.51	2.44	11.03	2.54	102.75
10	3000	715	2.51	2.43	11.00	2.95	88.51
10	4000	715	2.50	2.43	10.70	3.34	78.09

Fracture conductivity measured after etching by the Ultra Series FF-01 was significantly higher compared to that obtained with 15% hydrochloric acid with additives, when the leak off was set at 100 psi lower than the system pressure for all values of closure stress. It is worth mentioning that during the conductivity measurement, the conductivity values from 15% HCl with additives was unstable and so the rate of injection of brine had to be increased from 4 mL/min to 10 mL/min. It was left for one week to get all conductivity values. The results of the experiment for the Ultra

series FF-01 and 15% hydrochloric acid with additives are compared at different closure stress values in Figure 46.

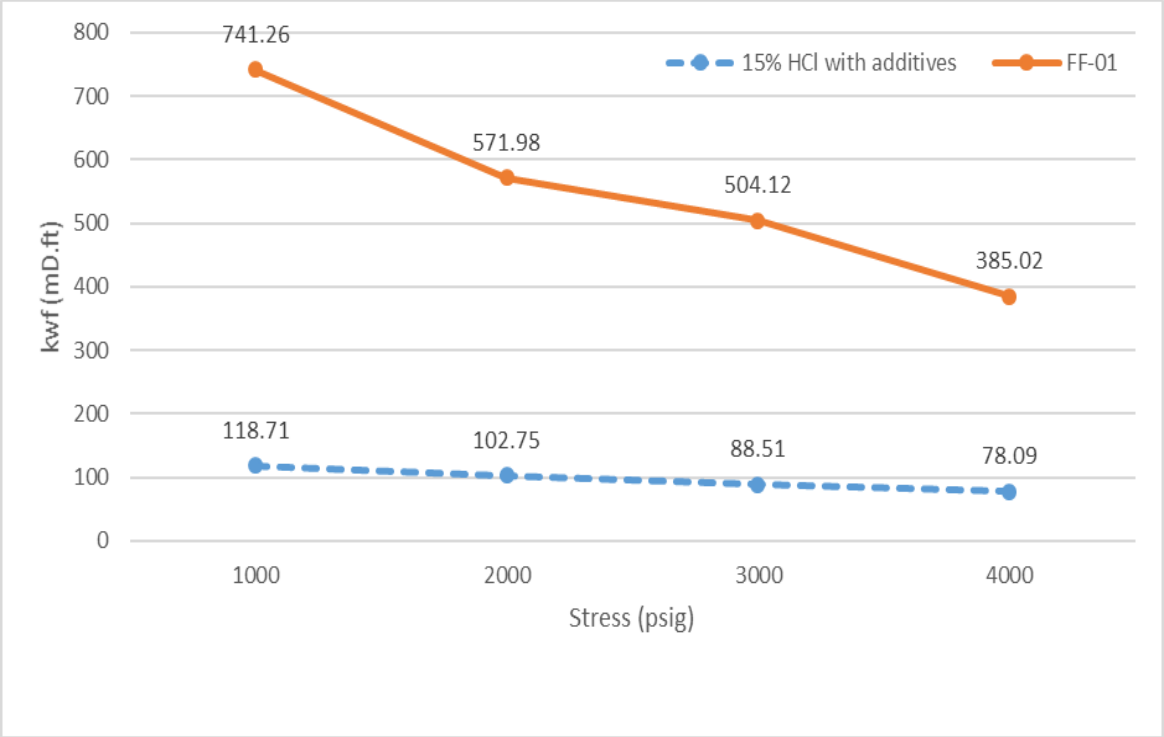

Figure 46: Fracture conductivity versus closure stress after acid fracturing (leak-off pressure is 100 psi lower than system pressure)

Figure 47 shows that the etching pattern that was created by the Ultra Series FF-01, was visible and connected. In contrast, the Figure 48 shows that the surface of the core samples that were etched by 15% hydrochloric acid with additives were bouncy but shallow, producing inferior conductivity. It was very evident from the difference in the etching patterns between the two fluids that the Ultra Series FF-01 is performing significantly better than the commercial 15% hydrochloric acid with additives.

Figure 47: Lueders Limestones surface (top core (top), bottom core (bottom)) were etched by the Ultra Series FF-01 when the leak off pressure was 100 psi lower than overall pressure.

Figure 48: Lueders Limestone surface (top core (top), bottom core (bottom)) were etched by 15% hydrochloric acid with additives when the leak off pressure was 100 psi lower than overall pressure.

In addition, one important factor during acid fracturing that can affect the result of the experiment is leak off pressure. Therefore, this experiment was repeated once more with the same injection rate, time of injection, and temperature but the leak off pressure was set at 50 psi lower that pressure system. Table 16 and Table 17 show the results obtained when the leak-off pressure was 50 psi below the fluid pressure.

Table 16: Experiment results where the FF-01 was used as a fracturing fluid and the leak off pressure was 50 psi lower than system pressure. An injection rate of 2 mL/min was used for a conductivity measurement.

Flow Rate mL/min	Stress (PSIG)	BPR (PSIG)	Top Cell - Ceiling (in)	Lower Cell - Floor (in)	Total Clearance (in)	Delta P (PSIG)	kWf (md* ft)
2	500	497	2.52	2.47	11.10	0.35	152.62
2	1000	497	2.51	2.46	11.08	0.41	130.94
2	2000	497	2.51	2.46	11.05	0.65	81.76
2	3000	497	2.51	2.45	11.05	0.91	58.35
2	4000	497	2.51	2.45	11.05	1.32	40.54

Table 17: Experiment results where the 15% HCl with additives was used as a fracturing fluid and the leak off pressure was 50 psi lower than system pressure. An injection rate for the conductivity measurement was 10 mL/min at the closure stress of 1000 and 2000 psig, then it was reduced to 2 mL/min at the closure stress of 3000 psig and 0.1 mL/min when the closure stress was increased to 4000 psig.

Flow Rate (mL/min)	Stress (PSIG)	BPR (PSIG)	Top Cell - Ceiling (in)	Lower Cell - Floor (in)	Total Clearance (in)	Delta P (PSIG)	kWf (md* ft)
10	1000	503	2.47	2.44	11.03	0.69	396.10
10	2000	503	2.47	2.44	11.02	4.29	63.43
2	3000	503	2.46	2.44	11.01	3.77	14.42
0.1	4000	503	2.44	2.44	11.00	4.21	0.65

The performance of the Ultra series FF-01 was slightly better than 15% hydrochloric acid with additives when the leak off pressure was set at 50 psi lower than the system pressure for all closure stress values except for the 1000 psi case. This may indicate that while the surfaces of the carbonate rocks were dissolved, the flow paths are not connected when the closure stress is high. Note that higher closure stressed of 2000 psi and above are more representative of the reservoir conditions. Also the rate of injection for 15% HCl with additives conductivity measurement was increased to 10 mL/min. However, once the closure stress was increased to 3000 psi, the pressure of the system increased more than 1500 psi, which is more than equipment capacity. The rate of injection was reduced significantly to 2 ml/min during conductivity measurement when closure stress was 3000 psi and 0.5 mL/min when the closure stress was 4000 mL/min. This may be due to the fact that

conductivity paths were closed when the closure stress was high. Figure 49 compares the conductivity values that were generated by 15% HCl with additives and the Ultra Series FF-01.

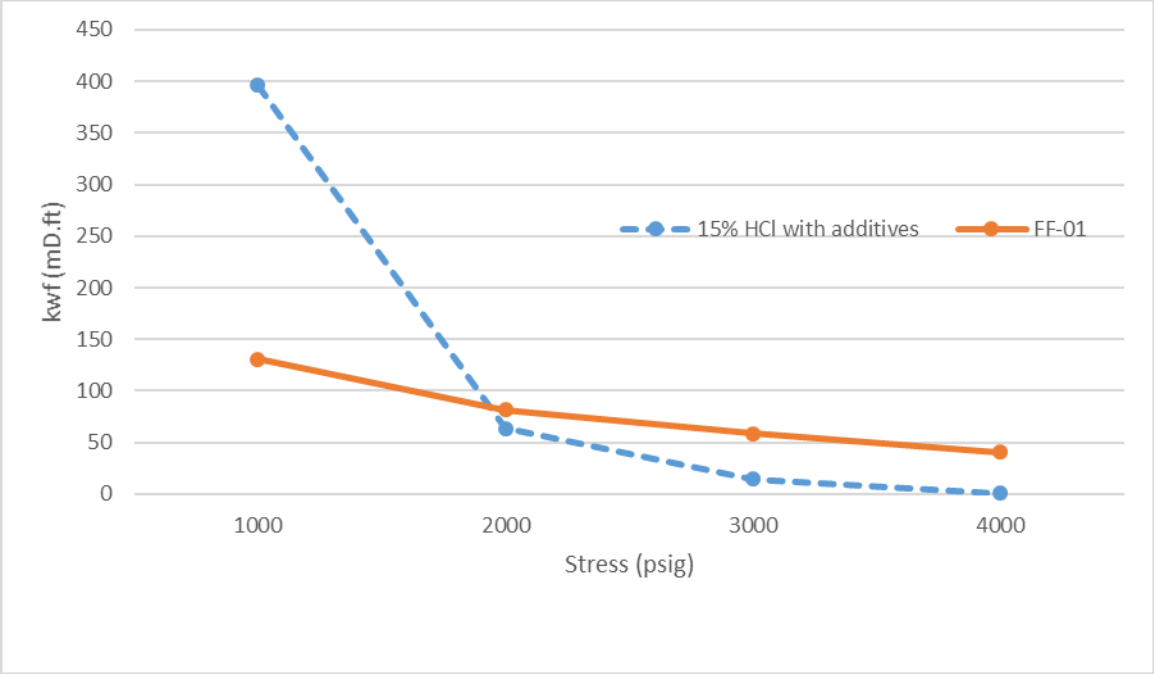

Figure 49: Fractured conductivity versus closure stress after acid fracturing (leak-off pressure is 50 psi lower than system pressure)

The thoughtful evidence of conductivity path after acid fracturing can be seen in Figure 50. The etching pattern that was generated by the Ultra Series FF-01 was in the shape of human veins, prominent, and connected. On the other hand, Figure 51 shows the surfaces which were etched by 15% HCl with additives, it is gritty but flat, and not connected.

Figure 50: Lueders Limestones surface (top core (top), bottom core (bottom)) were etched by the Ultra Series FF-01 when the leak off pressure was 50 psi lower than overall pressure.

Figure 51: Lueders Limestone surface (top core (top), bottom core (bottom)) were etched by 15% hydrochloric acid with additives when the leak off pressure was 50 psi lower than overall pressure.

5.7.2 Conductivity results of the acid-fracture conductivity measurement tests with reactor

Rate of reaction of 15% HCl, inevitably impacts the result of well acidizing as it is quickly spent at the entrance of the fracture. Thus, the reactor was added to the system. The additional reactor allows the acidizing fluid to meet and react with the carbonate powder first before it moves to the core sample. However, calcium carbonate powder clogged the injection line during the experiment. Therefore, the limestone cores were used in the reactor instead of calcium carbonate powder. Table 18 shows the results of fracture conductivity after the addition of the reactor when Ultra Series FF-01 was and Table 19 shows the results when 15% HCl with additives was used.

Table 18: Experiment results (with reactor) where the FF-01 was used as a fracturing fluid and the leak off pressure was 100 psi lower than system pressure. An injection rate of 2 mL/min was used for a conductivity measurement.

Flow Rate (mL/min)	Stress (PSIG)	BPR (PSIG)	Top Cell - Ceiling (in)	Lower Cell - Floor (in)	Total Clearance (in)	Delta P (PSIG)	kWf (md* ft)
2	500	475	2.49	2.48	11.09	0.25	213.60
2	1000	475	2.49	2.48	11.08	0.25	212.38
2	2000	475	2.49	2.48	11.08	0.27	201.48
2	3000	475	2.49	2.48	11.07	0.39	138.82
2	4000	475	2.48	2.47	11.07	0.64	84.09

Table 19: Experiment results (with reactor) where the 15% HCl with additives was used as a fracturing fluid and the leak off pressure was 100 psi lower than system pressure. An injection rate of 2 mL/min was used for a conductivity measurement.

Flow Rate (mL/min)	Stress (PSIG)	BPR (PSIG)	Top Cell - Ceiling (in)	Lower Cell - Floor (in)	Total Clearance (in)	Delta P (PSIG)	kWf (md* ft)
2	500	487	2.45	2.48	11.02	0.42	130.73
2	1000	487	2.44	2.47	11.02	0.71	76.37
2	2000	487	2.44	2.47	11.02	0.98	55.54
2	3000	487	2.43	2.47	10.98	2.14	25.49
2	4000	487	2.43	2.46	10.98	6.94	7.84

Results from the experiments show that fracture conductivity produced by the Ultra Series FF-01 is better than what was produced by the commercial 15% HCl with additives, at all closure stresses. The increase in the volume of spent acid reduces the ability of the commercial 15% HCl with additives to etch the surface of the carbonate rocks but at the same time it has only a slight impact

on Ultra Series FF-01. The results of conductivity measurement when the reactor was added for 15% HCl with additives and the Ultra Series FF-01 were compared in Figure 52.

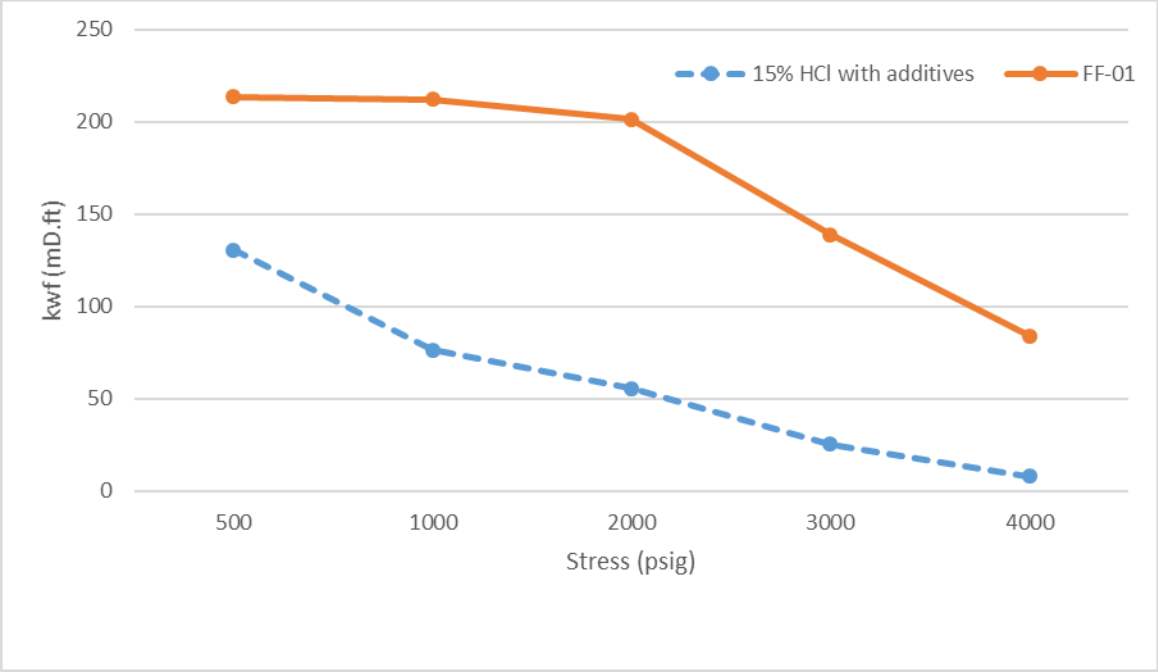

Figure 52: Fractured conductivity versus closure stress after acid fracturing with a reactor (leak-off pressure is 50 psi lower than system pressure)

The surface of the core samples after completion of the experiment using Ultra Series FF-01 are shown in the Figure 53. The etching is deep, connected and can be seen clearly. Conversely, the etching on the surface of carbonate rock samples using 15% HCl, are very shallow as can be seen in Figure 53.

Figure 53: Lueders Limestones surface were etched by the Ultra Series FF-01 (a reactor was added in the conductivity setup)

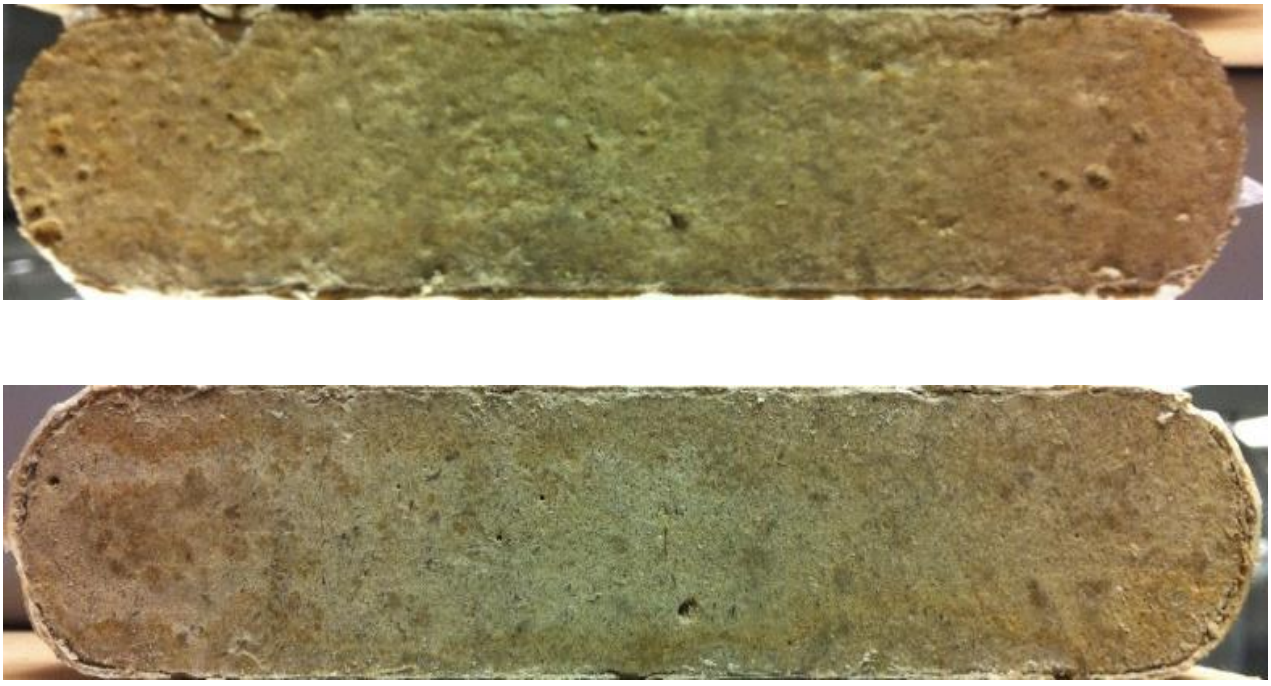

Figure 54: Lueders Limestone surface were etched by 15% hydrochloric acid with additives (a reactor was added in the conductivity setup)

Conclusions

The Ultra Series FF-01 was tested to explore its potential as an environment and equipment friendly alternative for conventional HCl acid used in acid fracturing of oil wells by comparing its performance with 15% hydrochloric acid with additives.

- From MSDS, the Ultra Series FF-01 has no hazardous chemical per OSHA standard. Moreover, it has no effect on human health even after exposure for an extended period of time.
- Under the guidelines of QCAT, the Ultra Series FF-01 is a safe chemical.
- The Ultra Series FF-01 is a safer product for our environment and most importantly to our health than a conventional acidizing fluid especially with its additives.
- The Ultra Series FF-01 is equipment friendly as the beaker test shows that there is no mass reduction in stainless steel rod after it was left in the Ultra Series FF-01 for 24 hours. The conventional 15 percent by weight HCl solution reduced the weight of the stainless steel rod.
- The viscosity at the interface of the Ultra Series FF-01 and the crude oil samples are lower than that of 15% HCl acid and 15% HCl acid with additives at all shear rates. The Ultra Series FF-01 reduced the viscosity of the crude oil sample it was tested against, and no emulsion or precipitation was formed.
- The Ultra Series FF-01 has a slower reaction rate than 15% HCl.
- The Ultra Series FF-01 does not create emulsion in LKC crude oil.
- The interfacial tension of the Ultra Series FF-01 increases as the concentration of the Ultra Series FF-01 decreases in the 2% KCl.

- 15% HCl with additives performed better during matrix acidizing. However, the Ultra Series FF-01 produced better results when compared with 15% HCl when a lower injection rate was used (0.5 mL/min) and the initial permeability was low (less than 5 mD)
- Acid conductivity measurement tests showed that the Ultra Series FF-01 generated higher conductivity than 15% hydrochloric acid when it was used for acid fracturing at all closure stress values when the difference between the leak off pressure and the overall pressure was 100 psi.

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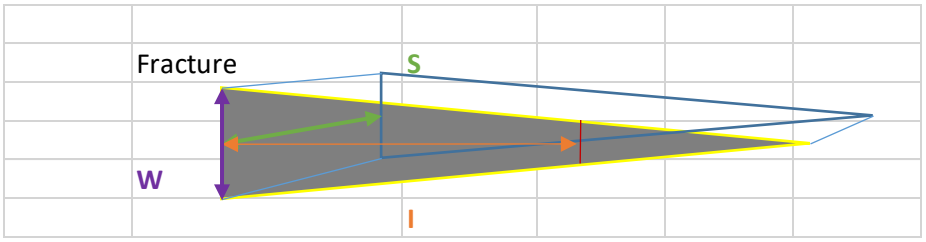
Appendix A

Calculating the amount of carbonate rock in the reactor.



Fracture dimension

Side (s) 15 ft

Length (l) 15 ft

Width (w) 0.25 in

Fracture surface area (s x l x w) 41.83 m^2

Carbonate powder

Particle size (d): 0.00003 m

Density 2.93 g/mL (ρ): @ 25 °C

Surface area (a): 2.83 x 10^{-11} m^2

Volume (v): 1.41 x 10^{-17} m^3

Thus,

Mass of single particle (v x ρ): 4.14 x 10^{-11} g

Mass of powder (mass of single particle x fracture surface area / surface area of carbonate powder): 61.29 g

From the beaker testing for the rate of reaction, we found that the ratio of the reaction rate of 15% HCl and $CaCO_3$ to the Ultra Series FF-01 and $CaCO_3$ is 3: 1. Thus the amount of the $CaCO_3$ powder used in the reactor for the fracture conductivity measurement with 15% HCl is three times more

than the amount of $CaCO_3$ powder used during the fracture conductivity measurement with the Ultra Series FF-01.

Appendix B

Equations in the model for calculating a percentage of acid spending of acid mixture introduced by Buijse, et al.

$$C = [H^+] + \sum_{i=1}^{N} \frac{[H^+] \cdot C_{0,j}}{[H^+] + K_{A,i}}$$

$$K_A = \frac{[Ca^{2+}] \cdot [CO_2 aq] \cdot 4\sqrt{X}}{[HA]}$$

$$R = k_f \cdot \left([H^+]_s^n - X^n \cdot \frac{(C_o - C_s)^{2n}}{[H^+]_s^n} \right)$$

$$K_A = \frac{[H^+] \cdot [A^-]}{[HA]}$$

Where:

C = acid concentration (mol/l)
C_0 = initial total acid concentration (mol/l)
K_A = acid dissociation constant (mol/l)
$K_{1,2,3}$ = equilibrium constants carbonic acid
R = dissolution rate (mol/cm^2/s)
s = surface
k = reaction rate constant
k_f = forward reaction rate constant